

***Cold Bench-Scale Test Report
for Chemical Oxidation/
Stabilization of Surrogate
V-Tank Waste at Waste Area
Group 1, Operable Unit 1-10***

**Idaho
Completion
Project**

April 2004

Bechtel BWXT Idaho, LLC

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April 2004


**Idaho Completion Project
Idaho Falls, Idaho 83415**

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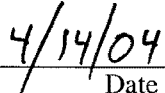
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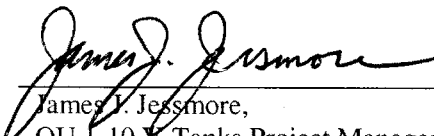
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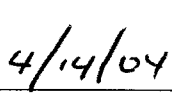
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ABSTRACT

Bechtel BWXT Idaho, LLC is planning remediation efforts for the V-tanks located at the Idaho National Engineering and Environmental Laboratory (INEEL) Test Area North, Waste Area Group 1, Operable Unit 1-10. Test Area North is one of ten Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (Ref. 1) waste area groups at the INEEL. Each of the four V-tanks—designated as Tanks V-1, V-2, V-3, and V-9—contains a combination of liquid and sludge that is contaminated with metals, organics, and radionuclides.

The information reported here will be used to determine whether it is reasonable to proceed with planned future laboratory studies on actual V-tank wastes, and to provide data to support title design and larger scale testing.

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ACRONYMS

AISI	American Iron and Steel Institute
ASTM	American Society for Testing and Materials
BBWI	Bechtel BWXT Idaho, LLC
BEHP	bis (2-ethylhexyl) phthalate
BP	biphenyl
BWXT	BWXT Services of Lynchburg, Virginia
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CFT	contaminant for treatment
COC	contaminant of concern
COP	chemical oxidation process
DI	deionized
DO	dissolved oxygen
DOE	U.S. Department of Energy
DRE	destruction and removal efficiencies
EPA	U.S. Environmental Protection Agency
GC	gas chromatograph
HCB	hexachlorobenzene
HDPE	high-density polyethylene
HKM	HKM Engineering, Inc.
ICDF	INEEL CERCLA Disposal Facility
IDL	instrument detection limits
INEEL	Idaho National Engineering and Environmental Laboratory
ISE	ion selective electrode
LCS	laboratory control standard
LDR	land disposal restriction

MS	mass spectrometer
MSE	MSE Technology Applications, Inc.
MV	method validation run
o/g	oil and grease
PCB	polychlorinated biphenyl
PCE	tetrachloroethylene
PCT	Portland Cement Type
QC	quality control
RCRA	Resource Conservation and Recovery Act
ROD	Record of Decision
RPD	relative percent difference
SOW	Statement of Work
SVOC	semi-volatile organic compound
TAN	Test Area North
TCA	1,1,1-trichloroethane
TCD	thermal conductivity detector
TCE	trichloroethylene
TCLP	toxicity characteristic leaching procedure
TO	test objective
TSF	Technical Support Facility
UFT	universal treatment standard
UTS	(RCRA) Universal Treatment Standards
VOA	volatile organic analysis
VOC	volatile organic compound
WAG	Waste Area Group

UNITS

accm	actual cubic centimeters per minute
Btu	British thermal unit
ca.	circa
cal	calories
cal/g	calories per gram
cal/min	calories per minute
cm	centimeter
g	gram
g/L	grams per liter
gal	gallon
gmin	grams per minute
gmol	grams per mole
gpm	grams per minute
hr	hour
in.	inch
K	degrees Kelvin
kcal/gmol	kilocalories per gram per mole
kg	kilogram
kJ/gm	kiloJoules per gram
K_{oc}/K_{ow}	organic carbon partition coefficient/octanol water partition coefficient
lb	pound
mg	milligram
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
mg/m ³	milligrams per cubic meter

min	minute
mL	milliliter
mm	millimeter
mv	millivolt
nm	nanometer
ppm	parts per million
ppmv	parts per million by volume
ppmw	parts per million by weight
psi	pounds per square inch
psia	pounds per square inch, absolute
rpm	revolutions per minute
sec	second
µg/L	micrograms per liter
µL	microliter

Cold Bench-Scale Test Report for Chemical Oxidation/Stabilization of Surrogate V-Tank Waste at Waste Area Group 1, Operable Unit 1-10

1. INTRODUCTION

Bechtel BWXT Idaho, LLC (BBWI) is planning remediation efforts for the V-tanks located at the Idaho National Engineering and Environmental Laboratory (INEEL) Test Area North (TAN), Waste Area Group (WAG) 1, Operable Unit (OU) 1-10. Test Area North is one of ten Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (Ref. 1) WAGs at the INEEL. Each of the four V-tanks—designated as Tanks V-1, V-2, V-3, and V-9—contains a combination of liquid and sludge that is contaminated with metals, organics, and radionuclides.

MSE Technology Applications, Inc. (MSE Technology) supported BBWI by performing a cold (i.e., nonradiological) bench-scale study using surrogates of V-tank waste. The overall goal of the cold bench-scale tests was to determine the conditions necessary for ex situ chemical oxidation followed by grout stabilization to meet onsite land disposal restrictions (LDRs) for organic and heavy metal contaminants for treatment (CFTs). Ex situ chemical oxidation followed by grout stabilization was selected from a list of seven candidate treatment options. The purpose of the cold bench-scale tests was to determine whether statistically significant destruction of CFTs could be achieved by ex situ chemical oxidation followed by grout stabilization and, if significant, to demonstrate the extent of that destruction and determine the efficiency of each oxidation reaction. This report summarizes the results of the cold bench-scale tests. The information reported here will be used to determine whether it is reasonable to proceed with planned future laboratory studies on actual V-tank wastes, and to provide data to support title design and larger scale testing.

1.1 Test Objectives

BBWI developed ten test objectives (TOs) for the cold bench-scale study.

1. TO 1—To determine which of the potential process scenarios are effective in treating surrogated V-tank waste to regulatory compliance levels, and to identify the most favorable conditions for the chemical oxidation process (COP) scenario for future pilot-scale testing and field deployment. Initial tests should be performed at the extreme ranges of the most aggressive conditions available to us, and at the minimal conditions that can be reasonably expected to produce results. This will establish bounds within which we can refine the effectiveness of the process.
2. TO 2—To determine conversion extent of CFT destruction in the COP. This objective and the following objectives are measurements to be made on both extremes of the process from TO 1, and at a limited number of suitable points in between.
3. TO 3—To estimate the rate of heat generation of the COP.
4. TO 4—To determine the bulk gas-generation rate of the COP.
5. TO 5—To estimate the durability of potential construction materials exposed to the COP.
6. TO 6—To estimate changes in leachability between raw waste and oxidized waste.

7. TO 7—To determine the sequence and relative extent of destruction.
8. TO 8—To propose, and provide data to support, a detailed strategy to prevent autocatalytic reactions for and Fenton's reagent during active remediation.
9. TO 9—To determine the behavior of volatile organic compounds (VOCs) in the off-gas; volatilization as opposed to destruction.
10. TO 10—To determine the completion of destruction of the Resource Conservation and Recovery Act (RCRA) (Ref. 2) hazardous organics and total organics, and to identify real-time methods for determining completion points.

Test Objective 1 of the bench-scale testing was the determination of “minimal” to “aggressive” operating conditions “that can reasonably be expected to produce the required results.” Initial studies identified safe operating conditions for surrogate waste treatment. The CFT destruction associated under these conditions was evaluated during the cold bench-scale study. Conditions for effective destruction/removal of the CFTs were identified.

Data quality was defined as screening level for the cold bench-scale study according to BBWI quality definitions. Organic and inorganic CFTs identified by BBWI were the focus of this study (see Table 1-1). More rigorous analysis and risk assessment activities are currently ongoing to verify that this list of CFTs best represents the compounds expected to drive destruction efficiencies to achieve regulatory compliance. Table 1-1 presents the CFTs and the U.S. Environmental Protection Agency (EPA) universal treatment standards (UTSs) (Ref. 3) for the CFTs in the stabilized slurry.

Table 1-1. Universal treatment standards for V-tank organic contaminants for treatment.

Organic Contaminant	Universal Treatment Standard (mg/kg)
Tetrachloroethylene (PCE)	6
Trichloroethylene (TCE)	6
1, 1, 1-Trichloroethane (TCA)	6
Arochlor-1260	10
Bis (2-ethylhexyl) phthalate (BEHP)	28

The reacted products were stabilized with one of two grout formulations. Grouted samples were cured at room temperature for 7 days and subjected to the toxicity characteristic leaching procedure (TCLP) for metals (Cr and Hg) and compressive strength testing to ensure that the solidified final waste form meets all UTSs for disposal. Grout formulations that produced acceptable stabilized waste forms were identified.

Preliminary beaker tests were completed to address TO 1 in Statement of Work, “V-Tank Bench-Scale Test Plan Scope of Work” (Ref. 4).

These tests consisted of varying surrogate composition, temperature, and the rate and amount of oxidizer addition. The results of the initial tests indicated the “most favorable” conditions of those evaluated for treatment of V-tank waste.

Although varying the mixing rate was included in SOW-615 as a variable under TO 1, the experimental setup prevented meaningful experiments for optimizing a mixing rate. Instead, the mixing rate used was not varied, but set at the maximum practical rate to ensure homogenization of the 1,000 mL flask contents.

The results from tests addressing TO 1 were used to define conditions for the cold bench-scale tests that addressed TOs 2–5 and 7–10. Test Objective 6—to estimate changes in leachability between raw waste and oxidized waste—was not addressed directly; however, a study was undertaken to evaluate two grout formulas for stabilization of the oxidized surrogate of V-tank waste. Test Objective 7—to determine the sequence of destruction—was not addressed in a rigorous way, but qualitative observations were made to see if the contaminants are destroyed before the oil phase.

Tests were executed to determine leachability of inorganic CFTs (Cr and Hg) from final grout stabilized waste forms. Some test objectives were edited to better reflect both the actual data to be collected and the conclusions that are possible, based on the current apparatus/experimental design. The cold bench-scale tests had the following objectives:

The cold bench-scale tests were designed to address the test objectives given above. The initial test plan anticipated a matrix of testing that included variation in initial run temperature, amount of hydrogen peroxide injected, and run time. As qualitative and quantitative results became available (i.e., when it became apparent that the product from the 40°C runs retained massively excessive peroxide and was unstable), the test design reverted to sequential testing with concurrence from the client for deviations from the test design.

Following the cold bench-scale tests, two additional definitive tests were performed to determine the effectiveness of subsequent chemical oxidation treatments. These definitive tests also provided more information about the destruction efficiency of the surrogate V-tank waste using Fenton's reagent, provided further data on volatilization of VOCs from the surrogate before and during reaction, and provided sufficient surrogate to allow intermediate sampling and reprocessing of the remainder. A section discussing these definitive tests was added to this report after completion of the first draft.

1.2 Overview of Fenton's Technology

The oxidation of organic matter using iron-catalyzed hydrogen peroxide (H_2O_2) was reported by H.J.H. Fenton in 1894. However, its utility as a treatment technology was not recognized until the reaction mechanisms were identified in the 1930s. Essentially, Fenton's reagent involves the following sequence (or cycle) of reactions:



In Equation 1, the hydroxyl radical (OH) is generated via reaction of ferrous ion (Fe^{+2}) and H_2O_2 . The OH radical is a powerful oxidation agent, being second only to fluorine (i.e., 2.06 versus 2.23-fold the oxidation power of molecular chlorine). In Equation 2, ferric ion (Fe^{+3}) reacts with H_2O_2 to produce the relatively weak perhydroxyl radical (OOH, i.e., 1.25-fold the oxidation power of Cl_2); however, this reaction stimulates further production of OH via Equation 1.

The OH and other free radicals associated with Fenton's will ultimately convert most hydrocarbons to water, carbon dioxide, and halide ions (if the parent compound is halogenated). Such conversions are dependent upon the following conditions:

- pH in the 3.0 to 4.0 range, to ensure relatively rapid reaction rates while maintaining iron in a soluble form (e.g., Fe^{+2})
- Maintaining appropriate $\text{Fe}:\text{H}_2\text{O}_2$ weight ratios (usually 1:5 to 15) to override inorganic/organic chelation effects (e.g., high phosphate or humic acid levels)
- Maintaining appropriate H_2O_2 :organic substrate weight ratios (usually $\geq 5:1$ mole:mole) and relatively strong H_2O_2 levels ($> 20 \text{ mg/L}$) to overcome scavenger reaction effects and maintain relatively high rates of OH production.

Upon completion of treatment, the reaction is quenched via cautious upward adjustment of pH (≤ 10) and careful monitoring of temperature changes ($\leq 50^\circ\text{C}$). Such conditions result in loss of catalyst (via precipitation of ferric oxyhydroxides) plus accelerated decomposition of H_2O_2 at elevated temperatures, without incurring thermal runaways at ca. 60°C .

Fenton's can be used for stand-alone, ex situ treatment of highly concentrated and/or toxic mixtures recalcitrant to biological treatment, as performed in publicly owned treatment works. In such cases, it can be applied to:

- Predigestion of low flows of wastewater(s) containing high levels of biological/chemical oxygen demand
- Enhanced performance of physical treatment processes, such as separation of entrained organics via improved flocculation of polar intermediate (Fenton's) reaction products.

More recently, Fenton's has been applied successfully to in situ treatment of a wide variety of contaminants in subsurface soils and groundwater. Such contaminants include fuel oils; benzene, toluene, ethyl benzene, and xylene (BTEX); chlorinated alkanes-alkenes-aryl compounds; pesticides; and MTBE.

It is anticipated that the reaction will proceed in a sequential manner with a series of intermediates, which are subject to further reaction. The desired end products are fully mineralized forms of carbon, hydrogen, and chlorine.

These tests are structured to provide the most general information possible. The nature of the process should lend itself to straightforward scale-up as far as destruction and removal efficiencies (DRE) are concerned. Engineering issues, such as heat transfer, will require a design staff.

2. METHODS AND MATERIALS DESCRIPTIONS

This section describes the chemical oxidation technology, surrogate composition, and the test apparatus.

2.1 Chemical Oxidation Technology Description

At the project's onset, a literature review pertaining to Fenton's-based oxidation of a wide variety of halogenated organic compounds (including polychlorinated biphenyls [PCBs] and dioxins) in both aqueous and soil/sediment matrices was performed. Based on this effort, it was determined that 50% by weight hydrogen peroxide (H_2O_2) and ferrous sulfate solution, initially containing approximately 2 g/L ferrous ion (Fe^{+2}), would be sufficient for treating the given V-tank surrogate.

2.2 Surrogate Composition

Bechtel BWXT Idaho, LLC, provided MSE Technology with the surrogate formulation to be used in the bench-scale study. The following tables describe the V-tank waste volume (Table 2-1), provide characterization data for the V-tank waste (Table 2-2), and provide the recipe for the V-tank surrogate (Table 2-3) that was used during the cold bench-scale study (Ref. 5).

Table 2-1. V-tank waste volume data (in gallons).

Tank	Capacity	Liquid Volume	Sludge Volume	Total Volume
V-1	10,000	1,164	520	1,684
V-2	10,000	1,138	458	1,596
V-3	10,000	7,660	652	8,312
V-9	400	70	250	320
Total	30,400	10,032	1,880	11,912

The V-tanks are four underground tanks that were installed at the TAN Technical Support Facility (TSF) in the early 1950s as part of a system designed to collect and treat radioactive liquid effluent. The purpose of Tanks V-1, V-2, and V-3 (designated TSF-09) was to store liquid radioactive waste generated at TAN before treatment. Tank V-9 (designated TSF-18) is a small clarifier for the liquid streams entering Tanks V-1, V-2, or V-3. Waste was pumped to these tanks from the TSF laboratories and craft shops, hot and warm shops, radioactive decontamination shop, hot cells, and the Initial Engine Test Facility. In 1968, a large quantity of oil, containing PCBs at 680 ppm, was discovered in Tank V-2, and the tank was subsequently taken out of service. The oil was removed from Tank V-2 in 1981, and the waste in all three tanks was removed in 1982. The tanks have not been used since the 1980s, although liquid was accidentally discharged to Tank V-3 in the late 1980s. The V-tank contents were sampled in 1993 and again in 1996.

Because the TSF-18 (Tank V-9) is contiguous with and received the same waste as TSF-09 (Tanks V-1, V-2, and V-3), the two sites have been combined for characterization and remedial analysis purposes (Ref. 6). Total volumes of tank contents are estimated at 1,880 gal of sludge and 10,032 gal of liquid. Table 2-1 breaks down the component quantities for a typical batch of V-tank surrogate.

Table 2-2. V-tank waste characterization data used in this study (Ref. 7).

Component	V-1	V-2	V-3	V-9	Expected Mean Concentration for Composite of V-tanks
Inorganics (mg/kg)					
Aluminum	527	1,120	923	2,690	483
Antimony	5.13	5.35	0.958	11.5	0.9
Arsenic	3.00	3.45	0.860	3.05	0.359
Barium	43.3	38	11.5	299	12.4
Beryllium	8.31	4.24	1.49	20.2	1.11
Cadmium	20.2	22.7	5.09	21.8	2.34
Calcium	1,780	2,240	2,340	6,750	1230
Chloride	208	102	59.9	397	106
Chromium	526	1,120	25.8	1,880	298
Iron	2,630	5,580	5,770	14,600	2670
Lead	255	303	72.6	454	36.1
Magnesium	2,640	2,240	3,470	9,010	1620
Manganese	702	2,230	1,150	4,270	749
Mercury	205	116	51.7	1,670	79.2
Nickel	81.4	76	23.8	319	16.4
Phosphorus	9,630	13,400	15,000	40,400	7260
Silicon	21,000	22,300	21,900	70,700	12300
Silver	35.2	50.5	6.95	522	18.4
Zinc	4,460	417	1,340	1,410	206
Volatile Organic Compounds (mg/kg)					
PCE	438	138	36.3	425	118
TCA	0.314	0.156	0.044	1770	52.2
TCE	3.85	0.362	0.216	14500	426
Semivolatile Organic Compounds (mg/kg)					
Bis (2-ethylhexyl) phthalate	919	586	338.0	345	454
Polychlorinated biphenyl (Arochlor-1260) or hexachlorobenzene and biphenyl	34.6	24.4	10.1	95.9	18
Radionuclides (nCi/g)					
Cesium	1,740	1,810	527.1	4,480	988
Strontium	1,520	3,200	1,499.2	5,180	1840
Transuranics	11	4.02	2.04	26.4	4.28
PCE = Perchloroethylene TCA = trichloroethane TCE = trichloroethylene					

Calculations performed on V-tank data concluded that the V-tank waste's radionuclide content could be segregated into two waste streams: (1) combination of Tanks V-1 and V-3, and (2) combination of Tanks V-2 and V-9. Table 2-3 summarizes the surrogate composition used for the cold bench-scale tests; CFT levels were based on the higher 95% upper confidence limit of the mean concentrations expected in the V-1/V-3 and V-2/V-9 waste combinations. The INEEL provided the formulation to MSE Technology. The higher 95% upper confidence limit concentrations were substantially derived from the V-2/V-9 combination. A total of 6,000 gal of liquid waste is present in the V-tanks. A final decision by BBWI has not been made regarding whether this waste will be decanted before treatment; however, the surrogate was developed assuming that the 6,000 gal of liquid will be removed. If the 6,000 gal of liquid is not ultimately decanted, the concentrations of CFTs in the waste requiring treatment will be much lower than concentrations used in the conservative surrogate formulation.

Table 2-3. Recipe for V-tank surrogate formulation.

Component	Weight % of Surrogate	Chemical Form	Molecular Weight	Atomic Weight	Grams used for 10-kg Surrogate Batch
Water	86.0	N/A	N/A	N/A	8,600
Hydraulic oil	1.50	N/A	N/A	N/A	150
Cutting oil	1.50	N/A	N/A	N/A	100
Aluminum	0.127	Al ₂ O ₃	102	27	23.99
Calcium	0.277	CaO	56	40	38.78
Chromium	0.114	Cr ₂ O ₃	152	52	16.66
Iron	0.653	Fe ₂ O ₃	159.7	55.85	93.36
Magnesium	0.314	MgO	40.3	24.3	52.08
Manganese	0.236	MnO	70.93	54.93	30.47
Silicon	2.81	SiO ₂	60.09	28.09	610.1
Phosphorus	1.66	Na ₃ PO ₄	164	31	878.2
Potassium	0.161	KOH	56.1	39.1	23.1
Mercury	0.037	N/A	N/A	N/A	3.7
Arochlor-1260	0.005	N/A	N/A	N/A	0.5
TCE	0.604	N/A	N/A	N/A	60.4
PCE	0.054	N/A	N/A	N/A	5.35
TCA	0.067	N/A	N/A	N/A	6.74
Bis (2-ethylhexyl) phthalate	0.116	N/A	N/A	N/A	11.6

Note 1: For selected tests, hexachlorobenzene and biphenyl were substituted for Arochlor-1260 to avoid unnecessary costs associated with procuring this reagent. MSE Technology believed that an inability to effectively destroy these substitutes would serve as a strong indicator that the system could not treat PCBs. Thus, the use of Arochlor-1260 was limited to the latter stages of the cold bench-scale tests.

Note 2: Total weight is above 10,000 g, due to oxygen in inorganic constituents.

PCE = perchloroethylene

TCA = trichloroethane

TCE = trichloroethylene

2.3 Surrogate Make-Up Procedure

The surrogate was made in a separate batch for each test to ensure that surrogate feed concentrations were accurate. The following procedure was used to make the surrogate.

An analytical balance is to be used to weigh the various quantities given below in Table 2-4 to the nearest 0.001 g. Table 2-5 shows the quantities of inorganic compounds used for V-tank surrogate.

Table 2-4. Quantities for a typical batch of V-tank surrogate.

Component	Grams (g)	Milliliters (mL)	Microliters (μL)
Charge:	150		
Water	120.0442	120.04	—
Hydraulic oil	2.0938	2.38	2,379
Cutting oil	2.0938	2.38	2,379
Al ₂ O ₃	0.3349	0.08	84
CaO	0.5413	0.16	163
Cr ₂ O ₃	0.2326	0.04	45
Fe ₂ O ₃	1.3032	0.44	435
MgO	0.7269	0.38	376

Table 2-4. (continued).

Component	Grams (g)	Milliliters (mL)	Microliters (μ L)
MnO	0.4254	0.08	82
SiO ₂	8.3907	3.71	3,713
Na ₃ PO ₄	12.2584	4.83	4,832
KOH	0.3224	0.16	158
Hg	0.0516	0.0038	3.8
Aroclor-1260	Varies for each test	—	—
TCE	0.8431	0.58	577
PCE	0.0747	0.05	46
TCA	0.0941	0.07	70
BEHP	0.1619	0.17	165
Total	150	135	—

Note: Hexachlorobenzene and biphenyl were occasionally substituted for Aroclor-1260.

Table 2-5. Quantities of inorganic compounds used for V-tank surrogate.

Compound	Grams	Compound	Grams
Al ₂ O ₃	0.3349	MnO	0.4254
CaO	0.5413	SiO ₂	8.3907
Cr ₂ O ₃	0.2326	Na ₃ PO ₄	12.2584
Fe ₂ O ₃	1.3032	KOH	0.3224
MgO	0.7269	Hg	0.0516

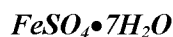
1. Water

- Weigh a 250-mL beaker on the semianalytical balance (0.001-g scale) and record its weight in the logbook.
- Fill a clean 100-mL graduated cylinder to the 100-mL mark with deionized water (DI) and pour into the 250-mL beaker, then add approximately 20 additional mL.
- Weigh the beaker and record its weight in the logbook. Set the beaker aside in the hood on a clean piece of weighing paper and cover it with a watch glass.

2. Inorganic Compounds

- Place a 50-mL beaker on the analytical balance and record its weight. Set the beaker aside on a piece of clean weighing paper and cover it with a watch glass.
- Weigh out the following inorganic compounds to the nearest 0.001 g with the analytical balance on individual weighing papers or weighing boats and add each sequentially to the 50-mL beaker.

- c. The elemental mercury can be sucked into a 5- μ L syringe and added to the flask. The syringe is to be weighed when charged with mercury and weighed after injection (see “Organic Compounds” section below for the general procedure for charging the flask with a syringe). Record the weights in the logbook.



- d. Weigh 1.500 ± 0.001 g ferrous sulfate heptahydrate on weighing paper using the analytical balance and add to the 50-mL beaker. Record the weight in the logbook.

3. Charging Water and Inorganic Compounds

- a. Remove the glass stopper from the reaction flask and place a powder funnel in the open neck.
- b. Carefully pour the inorganic compounds from the 50-mL beaker into the powder funnel using a rubber policeman to sweep the beaker.
- c. Pour approximately 20 mL of water from the 250-mL beaker into the 50-mL beaker and use the rubber policeman to clean any residue into the flask. Wash the powder from the sides of the funnel. Repeat this two more times.
- d. Retain approximately 20 mL of the water to wash the solid organic compounds into the reaction flask. Weigh the beaker after adding the solid organic compounds.
- e. Using the last of the water from the 50-mL beaker, wash the rubber policeman into the powder funnel before attempting to wash any remaining visible powder residue from the funnel into the flask.
- f. Remove the funnel from the neck of the flask and replace the ground-glass stopper.
- g. Weigh both the 50-mL and the 250-mL beakers and record their weights.
- h. Start the stirrer and mix contents at low speed in preparation for charging the organic compounds.

4. Organic Compounds

- a. The quantities of the organic compounds are listed below. The VOCs are to be stored in the refrigerator before the test in order to reduce volatilization.
- b. The VOCs will be charged to the reaction flask using appropriately sized syringes just prior to the initiation of the peroxide addition. The syringes are to be handled with nitrile (**not latex**) gloves during the filling, weighing, and charging operations. For oils, disposable pipettes will be used in a manner similar to the syringes. The pipettes are to be tared and weighed after injection to determine the net weight of the charged oil. The general technique for charging each compound is:
 - (1) Pour the selected compound from the reagent bottle into a clean and dry beaker or graduated cylinder of the appropriate size. The quantity of the compound should be slightly more than two times that required for the test.

- (2) As an alternative method, fill 40-mL volatile organic analysis (VOA) bottles with the VOCs and use syringes in the following manner:
- (a) From the beaker/cylinder or VOA bottle, fill the syringe to slightly greater than the approximate volume required for the test.
 - (b) Discharge the reagent from the syringe into a separate beaker for disposal to the hazardous waste pail.
 - (c) Refill the syringe, making sure there are no air bubbles in the syringe by tilting it upward and depressing the plunger. This may require discharging the syringe into a paper towel.
 - (d) Depress the syringe plunger to the volume line indicated for the test and touch the tip on the inside of the waste beaker to clear the end drop.
 - (e) Place a clean weighing paper on the analytical balance and tare it.
 - (f) Weigh the syringe on the analytical balance and record its weight in the logbook. (This step is to be used for the mass balance tests).
 - (g) Remove the ground-glass stopper from the neck of the flask and inject the compound from the syringe into the vortex created by the stirrer.
 - (h) Touch the tip of the injection needle to the side of the neck below the ground glass to clear the drop from the tip.
 - (i) Weigh the empty syringe on the analytical balance and record its weight.
 - (j) Clean the syringe by alternately filling and discharging acetone into the waste collection beaker. Do at least three flushes for the trace compound syringes.
 - (k) Dry the syringes by cycling the plunger with air several times.
 - (l) Store the dried syringes in a desiccator.
- c. Always use the same syringe for each separate compound. This may be done by storing the syringe in a marked beaker within the desiccator.

5. Gross Organic Compounds

Table 2-6 lists the quantities of gross organic compounds for the V-tank surrogate.

Table 2-6. Gross organic compounds.

Compound	Grams	mL	μL	Pipette Capacity (mL)	Quantity to Charge (mL)
Hydraulic oil	2.0938	2.38	2,379	2.5	2.38 ± 0.01
Cutting oil	2.0938	2.38	2,379	2.5	2.38 ± 0.01

Table 2-6. (continued).

Trace Organic Compounds (Contaminants of Concern).					
Compound	Grams	mL	μL	Syringe Capacity	Quantity to Charge
Aroclor-1260	None			10 μL	None
TCE	0.8431	0.58	577	1 mL	$0.58 \pm 0.01 \text{ mL}$
PCE	0.0747	0.05	46	100 μL	$46 \pm 0.1 \mu\text{L}$
TCA	0.0941	0.07	70	100 μL	$70 \pm 0.1 \mu\text{L}$
BEHP	0.1619	0.17	165	250 μL	$165 \pm 0.1 \mu\text{L}$

6. Solid Organic Compounds

- Some test runs will substitute hexachlorobenzene and biphenyl solids for Aroclor-1260. To approximate equivalent moles of chlorine, weigh out 0.0029 g biphenyl on a piece of tared and folded weighing paper and record its weight. Retare the balance. Weigh out 0.0056 g of hexachlorobenzene on a separate portion of the weighing paper. Place the weighing paper in a petri dish to transfer it to the reaction flask.
- Replace the powder flask on the neck of the reaction flask. Use a rubber policeman to brush the organic compounds into the flask, avoiding the walls of the funnel as much as possible.
- Use part of the remaining water to wash remaining compounds from the weighing paper and funnel into the reaction flask.
- Using the last of the water from the 250-mL beaker, wash the rubber policeman into the powder funnel attempting to wash any remaining visible powder residue from the funnel into the flask.
- Remove the funnel from the neck of the flask and replace the ground-glass stopper.
- Weigh both the 50-mL and the 250-mL beakers and record their weights.

7. Reactant Quantities

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$:	1.5 g (1.000 g per 100 g of waste charge).
H_2O_2 (50% w/w):	50-mL initial dose in 10 minutes followed by 2 mL per minute to specified total dose for a given test condition.
NaOH (4M):	As needed. At the beginning of the test, measure and record a weight of caustic sufficient for the test into a labeled beaker of appropriate size. At the end of the test, determine the quantity of caustic used to the nearest milligram. Record the strength of caustic used.
H_2SO_4 :	As needed. At the beginning of the test, measure and record a weight of acid sufficient for the test into a labeled beaker of appropriate size. At the end of the test, determine the quantity of acid used to the nearest milligram. Record the strength of acid used.

The major differences between the actual waste and the surrogate used for this testing are the conservatively high levels of CFTs to the surrogate and the fact that VOCs were not added to the surrogate until just before initiation of peroxide addition. This change was made following the early shakedown runs to avoid volatilization of these compounds during heating of the reaction flask contents before active treatment/gas sampling began. A test run after the formal runs to determine the impact of subsequent treatments on DREs included the VOCs in the original surrogate and gas sampling during the heating period.

2.4 Apparatus Description

The laboratory apparatus used for the cold bench-scale tests consisted of:

- 1,000-mL three-necked reaction flask connected to a circulating fluid bath (i.e., water for 40°C tests and silicone oil for 80°C tests)
- Reflux condenser with cooling water
- Dewar condenser
- Condensate receiver
- Glass adapters with syringe sampling septa for gas chromatograph (GC) analysis of the off-gas
- Classic bubble meter to measure noncondensable gas generation rate
- Miscellaneous adapters to fit the apparatus together.

Figure 2-1 illustrates the glassware setup. The equipment was capable of supporting all conditions and performed well throughout the testing.

The reaction flask has a nominal volume of 1,000 mL. The flask's initial reactant volume was approximately 150 mL of the surrogate mixture; the volume at the end of each experiment depended on the amount of oxidizer added and the reaction temperature.

The reaction flask was enclosed within an integral glass jacket that allowed temperature control of its contents with silicone oil, pumped from an isothermal bath. The temperature of the heat transfer fluid was measured entering and exiting the flask's jacket. The fluid's flow rate was measured by periodically timing its flow into a graduated cylinder. One of the reaction flask's necks was used to insert the pH probe for temperature and pH readings. PH control is necessary to facilitate reaction progress and minimize the risk of a runaway reaction.

The reaction flask's central neck was used to support an adapter that has two necks: the mixer shaft was inserted into one neck, and the reflux condenser was attached to the other neck. A paddle mixer was used to homogenize the contents of the reactor. Peroxide was fed to the flask through an adaptor on the third neck of the reaction flask. Headspace gas samples were collected every 30 min by inserting a long needle gas-tight syringe into the tubing used to deliver the pH adjustment reagents. The inlet and outlet temperatures of the reflux condenser cooling water were measured periodically; the water flow was measured by timing its rate into a graduated cylinder.

A tee adapter was placed on top of the reflux condenser. The straight arm of the tee held a septum for GC/MS gas analysis. The tee's other arm was extended to the Dewar condenser's inlet. A spherical joint was used in the middle of the extension to allow easier alignment of the apparatus.

The gas that flowed from the reflux condenser proceeded to the top of the Dewar condenser. The Dewar condenser was filled with an ice-water mixture. Condensate was collected in the condenser receiver.

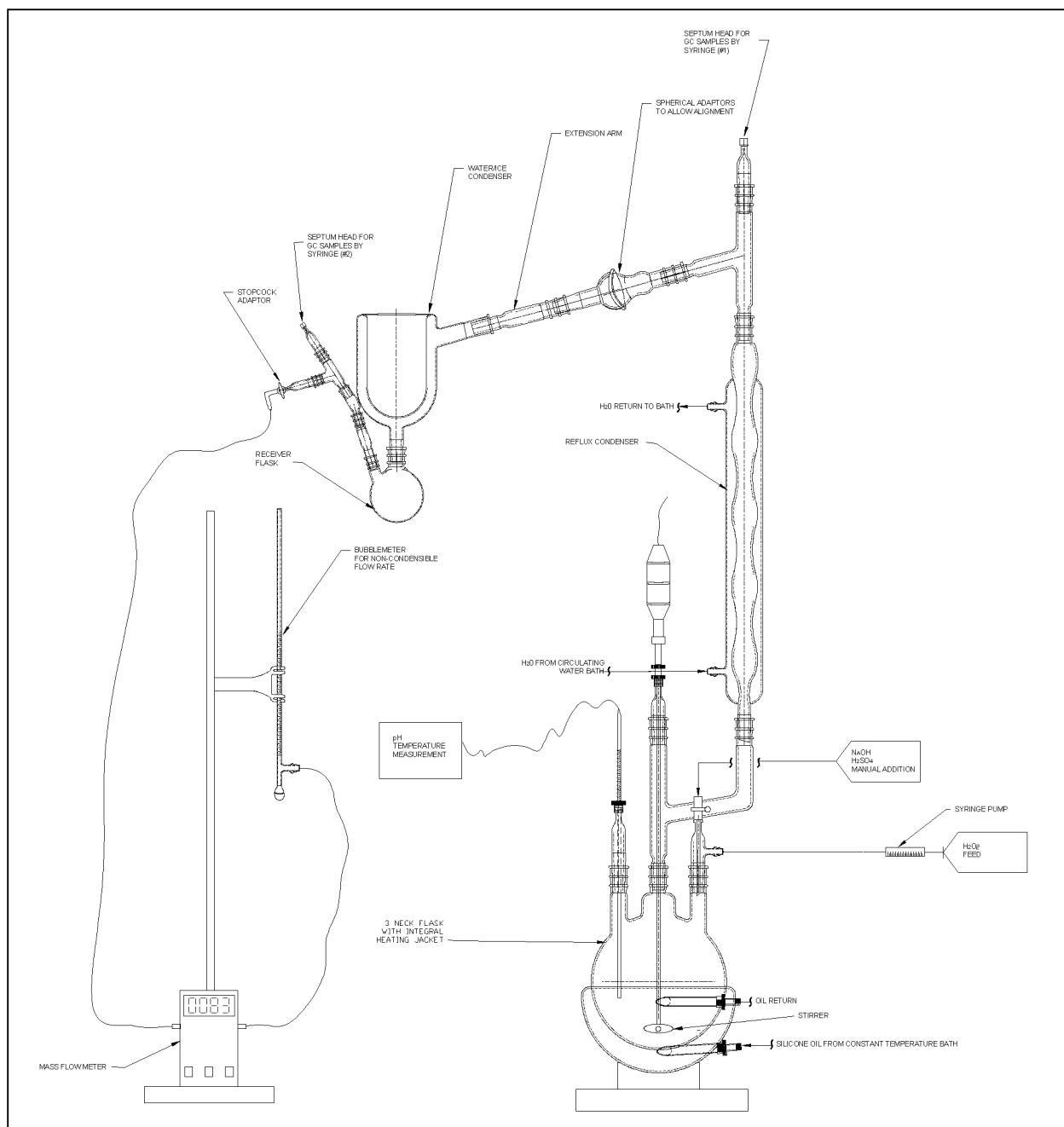


Figure 2-1. Test apparatus.

A photograph of the test apparatus can be found on Page 3 of Appendix F.

3. EXPERIMENTAL ACTIVITIES, RESULTS, AND DISCUSSION

This section presents a brief overview of the following test activities and discussion of the results from each activity:

- Chemical oxidation tests—addresses TO1, TO2, TO3, TO4, TO7, TO8, TO9, and TO10
- Stabilization of V-tank surrogate waste—addresses TO6 for oxidized waste forms
- Corrosion tests—addresses TO5.

3.1 Chemical Oxidation Test design

The experimental parameters for the cold bench-scale chemical oxidation test series included: starting reactor temperature (40 or 80°C), amount of oxidizer addition (150, 250, 400, 500, or 600 mL), and test duration (8 or 12 hr).

System pH was adjusted initially and then monitored and adjusted throughout treatment to 3.5 ± 0.5 by addition of concentrated (19N) sulfuric acid or 4N sodium hydroxide solution. The selected pH was identified as most favorable to reaction progress, and minimizes the risk of a runaway reaction. The following parameters were monitored:

- Reactor temperature
- Flow rate of noncondensable gases
- VOCs in the reactor headspace gas and at the outlet of the Dewar condenser
- Product slurry volume and weight at the end of each experiment
- Product concentrations of CFTs at the end of each experiment
- Weight and chemical analysis of condensate present in the condenser receiver at the end of each experiment.

The starting and ending concentrations of CFTs were used to calculate the experiment-specific DRE for each CFT. An overall mass balance was calculated for each test run. A summary of the data collected for each test is contained in Appendix A. Computational methods used with examples and estimates of uncertainty associated with each measurement are contained in Appendix B. Appendix C contains summaries of each test run taken from the project spreadsheet. Appendix D contains copies of the BWXT Services of Lynchburg, Virginia (BWXT) Analytical Data for the analysis of the reaction products for the CFTs. Appendix E contains copies of the HKM Engineering analytical data, which includes oil and grease, chloride and VOC data from the reaction products and the condensate when available. Appendix F contains selected photographs of the testing activities.

3.1.1 Shakedown

Shakedown runs were made before the formal chemical oxidation tests. The shakedown runs were designated:

- F1A—(80°C, 4 hr, 0 mL H₂O₂) which was used to provide gas samples for GC/MS analysis
- F1B—replicating F1A to provide liquid samples for initial VOC analyses

- F2A—(40°C, 8 hr, 400 mL H₂O₂) which was the first run with peroxide and used to confirm procedures and establish operating characteristics
- F4—(80°C, 8 hr, 400 mL H₂O₂) establishing operation at 80°C with peroxide and developing gas sampling procedures
- F5—(80°C, 8 hr, 500 mL H₂O₂) which further refined procedures and provided data for mass and energy balance calculations.

The reaction products from the shakedown runs were not analyzed for the CFTs, so no information existed about the effectiveness of the selected shakedown test conditions. The shakedown runs did, however, validate that the test apparatus would allow test runs at the identified test conditions. One of the major observations during shakedown was that the runs at 80°C appeared to have completely depleted the peroxide, while the 40°C run had substantial residual peroxide. When attempts were made to stabilize the 40°C product with caustic, the slurry foamed over as the pH was adjusted to 7. This suggests that a scaled-up process will have to be implemented to ensure depletion of peroxide by raising the temperature and driving it off as oxygen.

3.1.2 Cold Bench-Scale Test Results

A method validation (MV) test and 11 formal Fenton runs have been made in the 1,000 mL glassware apparatus. In each experiment, 150 g of surrogate were treated with Fenton's reagent. Table 3-1 summarizes the run designators and their target parameters from the experimental matrix.

Table 3-1. Summary of formal experiments performed to date.

Run Designator	Reactor Temperature	H ₂ O ₂ Volume Addition	Test Duration	Comments
Method Validation (MV)	80°C	0 mL	8 hr	Mass balance closure without peroxide addition (TCE, TCA, and PCE were the only CFTs in the surrogate).
F-6	40°C	500 mL	8 hr	
F-8	80°C	500 mL	8 hr	
F-9	80°C	400 mL	8 hr	
F-9A	80°C	500 mL	8 hr	Replicate of F-8
F-10	80°C	400 mL	12 hr	
F-12	80°C	500 mL	12 hr	
F-13	40°C	400 mL	12 hr	
F-16	80°C	500 mL	12 hr	Surrogate contained Arochlor 1260
F-20	80°C	150 mL	8 hr	
F-21	80°C	250 mL	8 hr	
F-22	80°C	600 mL	12 hr	Surrogate contained Arochlor 1260

Note: Tests F-1 through F-5 were shakedown tests. F-7 (40°C, 400 mL H₂O₂, 8 hr) was cancelled because the duration was too short for meaningful results at 40°C, based on preliminary results. F-11 (40°C, 500 mL H₂O₂, 12 hr) was cancelled and replaced with F-20 (80°C, 150 mL H₂O₂, 8 hr) because 40°C runs were ineffective based on available data. F-14 (80°C, 400 mL H₂O₂, 12 hr) and F-15 (40°C, 400 mL, 12 hr) were cancelled due to budgetary constraints. F-17 (40°C, 500 mL H₂O₂, 8 hr) was cancelled and replaced with F-22 (80°C, 600 mL H₂O₂, 12 hr).

The method validation run, with no peroxide added, produced samples to determine the amount of the VOCs in the surrogate that would leave the reactor charge due to vaporization and to allow an estimate of the variability to be seen in the organic analyses of the surrogate. Runs F8 and F9A were replicates. A summary of results for the formal experiments is presented in Table 3-2.

Table 3-2. Summary of selected results from the cold bench-scale tests.

Run Designator	Test Conditions	TCE DRE (%) (Conc. mg/kg) ^a UTS=6 mg/kg	TCA DRE (%) (Conc. mg/kg) ^a UTS=6 mg/kg	PCE DRE (%) (Conc. mg/kg) ^a UTS=6 mg/kg	BP DRE (%) (Conc. mg/kg) ^a	HCB DRE (%) (Conc. mg/kg) ^a	BEHP DRE (%) (Conc. mg/kg) ^a UTS=28 mg/kg	A1260 DRE (%) (Conc. mg/kg) ^a UTS=10 mg/kg	Average T° (°C)	Average Gas Flow Rate (g/min)	Mass Balance Closure	Residual Peroxide	Residual Oil and Grease (mg/L)
Method Validation (MV)	80°C, 0 mL H ₂ O ₂ , 8 hr	100% (<1.11 mg/kg)	99.7% (<1.98 mg/kg)	99.6% (<1.98 mg/kg)	N/A	N/A	N/A	N/A	79.9	0.11	89%	N/A	Not collected
F-6	40°C, 500 mL H ₂ O ₂ , 8 hr	99.0% (12.0 mg/kg)	99.7% (0.361 mg/kg)	91.7% (9.06 mg/kg)	— ^b	— ^b	— ^b	N/A	45.1	0.021	97.7%	>35%	Not collected
F-13	40°C, 400 mL H ₂ O ₂ , 12 hr	99.9% (1.19 mg/kg)	98.7% (<1.93 mg/kg)	94.1% (7.24mg/kg)	35.9% (3.31 mg/kg)	60.6% (3.63 mg/kg)	6.3% (250 mg/kg)	N/A	45.7	0.02	98.1%	>35%	Not collected
F-20	80°C, 150 mL H ₂ O ₂ , 8 hr	99.4% (18.65 mg/kg)	99.9% (0.287 mg/kg)	98.8% (2.96 mg/kg)	73.3% (<2.63 mg/kg)	72.3% (5.63 mg/kg)	65.9% (193 mg/kg)	N/A	84.9	0.09	97.5%	<2%	Not collected
F-21	80°C, 250 mL H ₂ O ₂ , 8 hr, surrogate included Arochlor 1260	99.96% (0.846 mg/kg)	99.1% (<1.96 mg/kg)	99.0% (<1.96 mg/kg)	47.7% (<4.70 mg/kg)	95.6% (0.777 mg/kg)	94.2% (24.3 mg/kg)	79.7% (2.6 mg/kg) ^c	86.2	0.15	97.3%	<2%/strip 0.04%	1,080
F-9	80°C, 400 mL H ₂ O ₂ , 8 hr	99.9% (<2.0 mg/kg)	97.9% (<2.0 mg/kg)	97.3% (<2.0 mg/kg)	N/A—broken samples	N/A—broken samples	N/A—broken samples	N/A	86.8	0.23	98.1%	<0.010%	Not collected
F-8	80°C, 500 mL H ₂ O ₂ , 8 hr	99.9% (<2.0 mg/kg)	98.7% (<2.0 mg/kg)	98.4% (<2.0 mg/kg)	N/A—broken samples	N/A—broken samples	N/A—broken samples	N/A	86.5	0.27	96.6%	<2%/strip <100 mg/L	Not collected
F-9A	80°C, 500 mL H ₂ O ₂ , 8 hr	99.9% (<1.91 mg/kg)	98.8% (<1.91 mg/kg)	98.4% (<1.91 mg/kg)	9.0% (<4.41 mg/kg)	53.0% (<4.41 mg/kg)	91.1% (23.5 mg/kg)	N/A	86.9	0.28	98.7%	<2%/strip 1,000 mg/L	Not collected
F-10	80°C, 400 mL H ₂ O ₂ , 12 hr	99.9% (<1.96 mg/kg)	98.9% (<1.96 mg/kg)	98.6% (<1.96 mg/kg)	14.8% (<4.86 mg/kg)	74.3% (2.93 mg/kg)	87.1% (42.5 mg/kg)	N/A	88.5	0.15	99.0%	<2%/strip 0.3% average	Not collected
F-12	80°C, 500 mL H ₂ O ₂ , 12 hr	99.9% (<1.93 mg/kg)	98.7% (<1.93 mg/kg)	98.3% (<1.93 mg/kg)	15.7% (<4.46 mg/kg)	91.4% (0.877 mg/kg)	82.2% (46.4 mg/kg)	N/A	86.1	0.19	97.6%	<2%/strip 0%	Not collected
F-16	80°C, 500 mL H ₂ O ₂ , 12 hr, surrogate included Arochlor 1260	99.9% (<1.95 mg/kg)	98.5% (<1.95 mg/kg)	98.4% (<1.95 mg/kg)	0.38% (<4.82 mg/kg)	71.5% (2.76 mg/kg)	89.4% (28.5 mg/kg)	92.7% (1.6 mg/kg) ^c	89.1	0.20	98.2%	<2%/strip 0.1%	2,740
F-22	80°C, 600 mL H ₂ O ₂ , 12 hr	99.9 (<1.70 mg/kg)	98.5 (<1.97 mg/kg)	98.6 (<1.50 mg/kg)	0% (<4.84 mg/kg)	72.4% (<2.72 mg/kg)	89.0% (25.8 mg/kg)	89% (6.6 mg/kg) ^c	90.0	0.24	99.9%	<2%/strip 200-400 mg/L	546

a. The concentrations of CFTs shown in parentheses do not account for the final grouting step required to demonstrate LDR compliance. It is estimated that these concentrations would be reduced by a factor of three (approximately) when the reaction products are combined with the grout materials.

b. Peroxide in samples for F-6 (40°C, 500 mL H₂O₂, 8 hr) boiled out in transit, concentrating the semivolatile organic compound (SVOC) samples; therefore, SVOC DREs calculated for run F-6 (40°C, 500 mL H₂O₂, 8 hr) were not accurate.

c. The amount of Arochlor 1260 charged to the reactor was different for each test due to difficulty making quantitative transfers from the vial. For test F-21 (80°, 250 mL H₂O₂, 8 hr), approximately 5 mg was added to the reactor. For test F-16 (80°C, 500 mL H₂O₂, 12 hr), 13.5 mg of Arochlor 1260 was used. For test F-22 (80°C, 600 mL H₂O₂, 12 hr), 42.8 mg was added to the reactor prior to the test.

3.1.3 Destruction and Removal Efficiencies

To address TO2, TO7, and the first part of TO10, DREs were calculated for CFTs in each test run. DREs were calculated using the mass of CFT added prior to the test and in the reaction products; therefore, no credit was taken for dilution of the reaction products with peroxide. Sample containers for the semivolatile organic compounds (SVOCs)—BEHP, hexachlorobenzene (HCB), and biphenyl (BP) from the F-8 and F-9 (80°C, 400 mL H₂O₂, 8 hr) runs were broken in transit to the laboratory. The cause of this breakage is still unclear, but all other samples were received at the laboratory intact. Results for SVOCs analysis from a replicate of test F-8 (test F-9A (80°C, 500 mL H₂O₂, 8 hr)) are available. The calculation used to calculate DREs is given below:

$$\text{DRE} = 100\% (1 - M_{\text{CFT } f} / M_{\text{CFT } i})$$

$M_{\text{CFT } f}$ is the mass of the compound in the products of the reaction. The mass is determined by the concentration of compound as analyzed by BWXT and by the mass of the product slurry as measured by MSE Technology personnel:

$$M_{\text{CFT } f} = [\text{CFT}] M_f / (1,000 \text{ g/kg})$$

The concentration of the contaminant for treatment (CFT) is in units of milligrams of compound per kilogram of final product (mg/kg). The mass of the product slurry, M_f , is in grams. The reported quantity of the CFT is in units of total milligram in the product slurry.

$M_{\text{CFT } i}$ is the amount of compound charged to the reaction flask. Each volatile and semivolatile compound that is charged to the reaction flask is weighed on an analytical balance using weighing paper, weighing boats, or microliter syringes.

The DRE determination for each CFT is then based on the weight charged to the reaction flask, the final product weight, and the analysis of the compound (ppm_w) in the product slurry. The equation expressing this result is, then:

$$\text{DRE} = 100\% \{1 - ([\text{CFT}] M_f / (1,000 \text{ gm/kg})) / M_{\text{CFT } i}\}$$

For SVOCs, the above equation calculates both the DRE and percent conversion of the compound during the course of reaction. For VOCs, the equation calculates the DRE, but not necessarily the conversion, by reaction. Conversion of volatile compounds has to take into account the loss of volatiles from the reaction flask by volatilization. Table 3-2 summarizes DREs calculated for test runs and other selected data. It should be noted that the concentrations of CFTs used to calculate DREs do not account for the addition of grout to create the final waste form. It is estimated that the concentrations of CFTs would be further reduced by a factor of three after the addition of grout at a ratio of 1:2 (waste:grout) mix.

The following paragraph addresses TO2, which is to determine conversion extent of CFT destruction in the chemical oxidation process. This objective and the following objectives are measurements to be made on both extremes of the process from TO1, and at a limited number of suitable points in between. The DREs for TCE, TCA, and PCE decrease in the same order as their respective Henry's Law coefficients (TCE 0.02>TCA 0.01>PCE 0.008), regardless of dosing and treatment time. This suggests that physical removal by volatilization exerts a greater effect than the chemical destruction by oxidation/bond-breakage. The relatively high DREs for BEHP and HCB may be due to breakage of at least one polar bond (i.e., C-O, C-Cl, respectively); thus these compounds are reduced in concentration, but not necessarily mineralized (i.e., converted to mono-ester of phthalic acid and tri-through penta-chlorobenzenes). The lighter components have higher vapor pressures favoring vaporization, but

their simple structures may react more easily as well. This cannot be distinguished by the test results. For selected runs, BWXT performed qualitative scans for all compounds present. The results from these runs indicated the presence of the intermediate compounds mentioned above. Biphenyl may be the most resistant to attack because of the even distribution of π bond charge throughout the ring structures (i.e., it appears to be difficult for the hydroxyl radicals to “open up” the ring).

Based on data from the 80°C test runs (F9A, F10, and F12), the relative extent of destruction (%DRE) for the target compounds (TO7) is as follows: VOC (97.3 to 100%)>BEHP (73.3 to 94.2%)>HCB (53.0 to 95.6%)>>BP (0 to 73.3%). Assuming an excess of free radicals, the sequence of reaction(s) with the SVOCs may be due to the “mechanisms” proposed above to address TO2.

As discussed in TO2 and TO7, it is presently impossible to quantitate the degree of chemical destruction versus physical volatilization of the three VOCs of regulatory concern (TO10). Because DREs for TCE, PCE, and TCA for all runs are high, including the MV run (with no active treatment), it appears that the VOCs can be effectively removed from the surrogate matrix under the 80°C test conditions. All VOC results to date in the reaction products have been reported as “U” (analyte not detected). The associated quantitation limits were used in the DRE calculations. It is hypothesized that the majority of VOCs are volatilized in the early part of the test after peroxide is added and gas generation begins. The B-1 series tests explored this question further (Section 3.2) and INEEL is modeling the expected behavior of VOCs in the system.

In addition, the data set for SVOCs of concern is limited to BEHP and Arochlor 1260. Table 3-3 presents BEHP results while Arochlor 1260 data are presented in Table 3-4.

Table 3-3. Summary of BEHP data.

Test Run	Test Conditions	Sample 1		Sample 2		Mean \pm Standard Deviation (mg/kg)
		Results (mg/kg)	Re-extraction Results (mg/kg)	Results (mg/kg)	Re-extraction Results (mg/kg)	
F-13	40°C, 400 mL, 8 hr	309	N/A	190	N/A	249
F-20	80°C, 150 mL, 8 hr	190	N/A	195	N/A	193
F-21	80°C, 250 mL, 8 hr	22.8	N/A	25.7	N/A	24.3
F-10	80°C, 400 mL, 12 hr	14.7	28.5	13.2	56.5	28.2 \pm 20.1
F-12	80°C, 500 mL, 12 hr	21.0	52.4	19.2	40.4	33.2 \pm 16.0
F-9A	80°C, 500 mL, 8 hr	9.90	26.4	13.5	20.6	17.6 \pm 7.4
F-16	80°C, 500 mL, 12 hr	29.5	N/A	27.4	N/A	28.5
F-22	80°C, 600 mL, 12 hr	33.8	N/A	17.7	N/A	25.8

Table 3-4. Arochlor 1260, HCB, and BP results.

Test Run	Test Conditions	Arochlor 1260 Concentration in		HCB Concentration in		BP Concentration in	
		Surrogate (mg/kg)	Reaction Products (mg/kg)	Surrogate (mg/kg)	Reaction Products (mg/kg)	Surrogate (mg/kg)	Reaction Products (mg/kg)
F-21	80°C, 250 mL, 8 hr	33.3	2.6	45.9	0.78	23.3	<4.70
F-16	80°C, 500 mL, 12 hr	89.7	1.6	39.9	2.76	19.9	<4.82
F-22	80°C, 600 mL, 12 hr	285	6.6	45.9	<2.72	21.3	<4.84

Note: The concentration of Arochlor 1260 varied for each test due to difficulty making quantitative transfers from the Arochlor 1260 container.

For tests F9A (80°, 500 mL, 8 hr), F-10 (80°C, 400 mL H₂O₂, 12 hr), and F-12 (80°C, 500 mL H₂O₂, 12 hr), SVOC samples were reextracted, thereby creating four values for these tests. Only two values are available for other test conditions. DREs for tests F9A, F-10 (80°C, 400 mL H₂O₂, 12 hr), and F-12 (80°C, 500 mL H₂O₂, 12 hr) were calculated using the more conservative values from the reextracted samples. The BEHP levels in the Sample 1/Sample 2 data sets are less than or equal to half those reported in the reextraction data sets. This difference is probably due to the lower, but still acceptable surrogate recovery results in the Sample-1/Sample-2 data sets; the effects of sample heterogeneity are also evident in F10, wherein the reextraction results vary by a factor of two. Nevertheless, the overall result indicates marginal compliance with the 28 mg/kg level set in the UTSs for land disposal of hazardous waste (40 CFR 268.48). At 40°C (test F-13 [40°C, 400 mL H₂O₂, 12 hr]), BEHP is above the UTS limit by a factor of nine. A chart of BEHP concentrations for 80°C tests is depicted in Figure 3-1. From Figure 3-1, it is evident that at least 250 mL of peroxide is necessary before the concentration of BEHP in the reaction product will achieve marginal compliance with the UTS limit. It is also evident from the BEHP results that the reaction product is heterogeneous and difficult to homogenize for sampling purposes, causing variability in results for field duplicate samples.

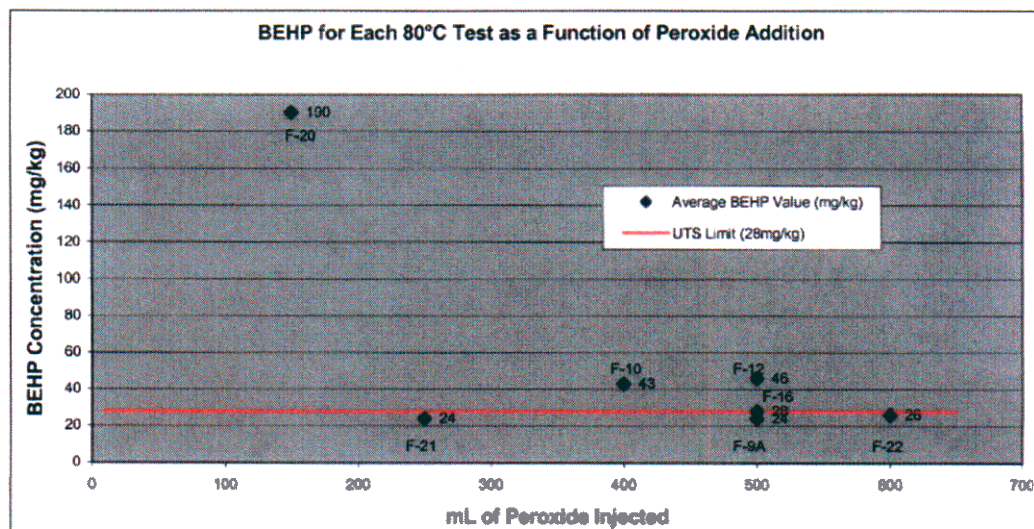


Figure 3-1. BEHP concentrations for 80°C tests.

It should be noted that the concentration of BEHP in the surrogate (~1100 mg/kg) is more than twice the average concentration in the actual waste (454 mg/kg). Also, the BEHP concentrations are based on the chemical oxidation reaction products and do not account for the addition of grout materials to create the final waste form for disposal.

While two samples were consistently collected and submitted to the laboratory for SVOCs analysis, only one sample was submitted for Arochlor 1260 analysis (often due to limitations in the surrogate volume available for sampling). Only the following runs included Arochlor 1260: Test F-21 (80°C, 250 mL H₂O₂, 8 hr), Test F-16 (80°C, 500 mL H₂O₂, 12 hr), and Test F-22 (80°C, 600 mL H₂O₂, 12 hr). Table 3-4 summarizes the Arochlor results.

Photos of the Sample F-16 (80°C, 500 mL H₂O₂, 12 hr) and F-22 are presented on page 2 of Appendix F.

All of the Arochlor 1260 data indicates that the concentration in the reaction products is below the UTS limit of 10 mg/kg under the selected test conditions. The final fate of the Arochlor 1260 is unclear, i.e., the reaction products of the partial destruction of Arochlor 1260 are unknown compounds. Follow-on tests indicate that total PCBs will be below the UTS limit. Figure 3-2 shows a chart of concentrations for Arochlor 1260.

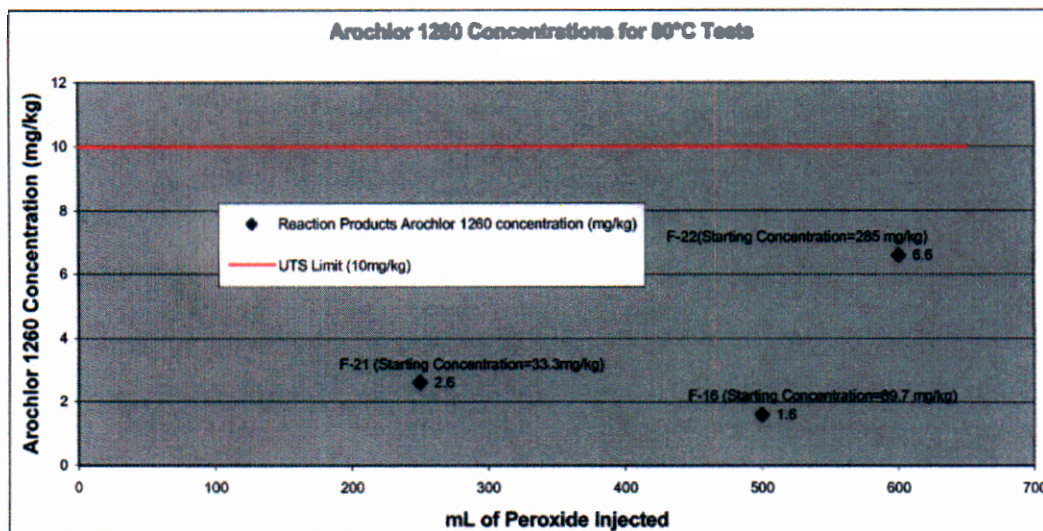


Figure 3-2. Archlor 1260 concentrations vs. volume of peroxide injected.

In all tests, BP and HCB were added to the surrogate to predict the behavior of PCBs in the system (EPA uses HCB and BP for PCB surrogates). BP was not added in high enough quantities to be detectable upon analysis of the reaction products; therefore, it is difficult to determine how much was actually destroyed. HCB was not as easily destroyed when compared to the Arochlor 1260, and therefore provided a conservative substitute for Arochlor 1260. As HCB has a UTS limit of 10 mg/kg like PCB, the reaction products indicate that HCB was removed to below this limit.

3.1.4 Heat Balance

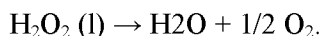
Test Objective 3, "Estimate the rate of heat generation of the COP," was approached by performing a complete heat balance around the glassware apparatus. The heat generated by reaction in the 1,000-mL flask was set equal to the heat added to the flask by the silicone oil pumped from a constant temperature bath, minus the heat lost through the reflux condenser and through the glass surfaces of the flask, minus the enthalpy of the peroxide pumped into the flask to effect reaction.

For the runs made with the initial temperature around 80°C, the average heat generation rate measured was -450 calories per minute for the overall run. A more useful heat generation rate may be for times when peroxide was being injected only; these rates average -846 calories per minute for the data taken when 2 mL peroxide per minute was being injected. From the accuracy estimated for the rate of heat generation, the value range when peroxide is being injected is -340 to -1,350 calories per minute.

For reasons explained below, a value of more than about –600 calories per minute is suspect. However, a heat generation value as high as –3,400 calories per minute when 5 mL of peroxide per minute is being injected could occur, unless initiation lag time inhibits the generation of heat.

The 40°C run shows much less heat generation, substantially less than –200 calories per minute. At 40°C, however, there appears to be a danger of runaway due to the high concentration of residual hydrogen peroxide. Any future tests at 40°C should use much lower peroxide injection quantities and run until gas and heat generation ceases.

The maximum amount of heat that can be generated by Fenton's reaction can be estimated. At 80°C, hydrogen peroxide decomposition is the predominate reaction:



The heat of formation of peroxide is –45.16 kcal/gmol, and the heat of formation of water is –68.3174 kcal/gmol, thus the heat of reaction for the decomposition is:

$$\Delta H^\circ_r = -68.3174 \text{ kcal/gmol} - (-45.16 \text{ kcal/gmol}) = -23.2 \text{ kcal/gmol H}_2\text{O}_2.$$

Per gram of peroxide, this is equivalent to, $\Delta H^\circ_r = -681 \text{ cal/g}$.

During a typical run, about 300 g of peroxide is charged. The maximum heat that can be generated by 300 g of peroxide is:

$$\Delta H^\circ_r = -681 \text{ cal/g} \cdot 300 \text{ g H}_2\text{O}_2 = -204,000 \text{ cal}.$$

If a run generates gas for 6 hr and totally decomposes peroxide to oxygen, then the rate of heat generation could be:

$$\Delta H^\circ_r = -204,000 \text{ cal} / (6 \text{ hr} \cdot 60 \text{ min/hr}) = -568 \text{ cal/min}.$$

About 4 g of various oils are charged to the reaction flask. For a typical hydraulic oil, the heat of combustion is about 46 kJ/g, or about 11,000 cal/g (19,800 Btu/lb). The heat released by the combustion of this oil should be about:

$$\Delta H^\circ_c = 4 \text{ g} (11,000 \text{ cal/g}) = 44,000 \text{ cal}.$$

Over the course of six hours, oxidation of the oil should release about $44,000/6/60 = 122 \text{ cal/min}$.

Therefore, during the course of a typical V-tanks run, the heat released from the reactor should be somewhere between 122 and 568 cal/min, depending on the combination of oxidation of the oil and decomposition of the peroxide that occurs at the reaction conditions. As shown above, the overall average for the runs made at 80°C, –450 cal/min, is within the range estimated by thermodynamics, and the average during injection of about –850 cal/min could be explained by decomposition, depending on the concentration of peroxide in the reactor at the time when the heat balance was made. The uncertainty in the heat generation number, however, makes it only useful to bound design estimates.

No attempt has been made to tie the rate of heat generation to the extent of conversion of the various reactants. A useful number for design may be the ratio of heat generation rate to the mass existing in the flask at the time of the heat balance. For example, during run F-16 (80°C, 500 mL H₂O₂, 12 hr) at 10:50, the reaction mass in the flask was about 578 g. The measured heat generation rate of -996 cal/578 g/min would give a mass normalized rate of -1.7 cal/g/min. If based on the average generation rate during injection, the estimate becomes -850/578, or -1.5 cal/g/min.

Appendix G describes the methods used to estimate the heat generated by reaction, and documents the data collected during the test campaign.

3.1.5 Bulk Gas Generation/Characterization

To address TO4 (to determine the bulk gas-generation rate of the COP), gas flow rate data was collected every 15 minutes during each test. Gas flow rates for the duration of each test are shown in Figure 3-3. Gas generation profiles for 80°C tests indicate high gas-generation rates while peroxide is being added to the reaction vessel. The flow then tapers off until, by the end of the test, there is virtually no gas being generated. For the 40°C runs, the gas generation rate is an order of magnitude less than 80°C runs and is more constant throughout the test. In fact, a small amount of gas was still being generated the morning after each of the 40°C runs.

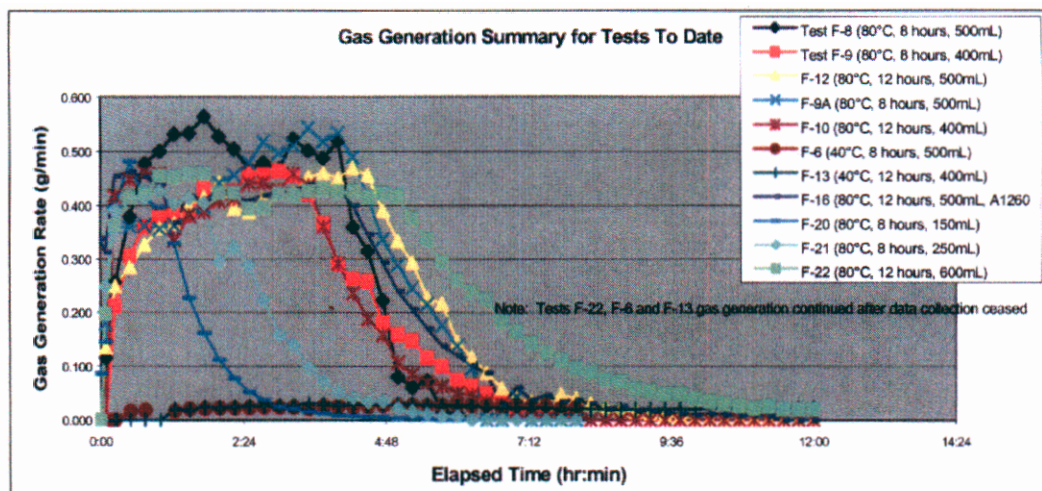


Figure 3-3. Gas generation profiles for cold bench-scale tests.

The gas generation rate from the reactor during the 80°C runs increased as peroxide was injected, and averaged about 0.2 g/min throughout each run, with high averages during peak injection periods being near 0.5 g/min. The peroxide injection rate for each run was 50 mL injected in the first 10 min, followed by 2 mL/min to the total of 400 or 500 mL of total peroxide injected.

If 2 mL/min of peroxide totally reacts to oxygen and does not oxidize surrogate material ($\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + 1/2 \text{O}_2$), about 0.565 g of oxygen would be generated per minute. The test results for the 80°C runs indicate that a very high fraction of peroxide reacts to oxygen and is lost through the gas phase, i.e., the peroxide utilization efficiency may be low for the 80°C runs. Within an hour after the completion of peroxide injection during the 80°C tests, gas generation slowed and flow rates were essentially zero near the end of the run (probably indicative of depletion of peroxide). Gas generation during the 40°C

runs, to date, averaged 0.021 gpm for both F-6 (40°C, 500 mL H₂O₂) and F-13 (40°C, 400 mL H₂O₂, 12 hr).

Originally, the following compounds were to be analyzed by GC/MS: oxygen, carbon dioxide, water, TCE, TCA, and PCE. After initial tests, water appeared to be saturated on the column and therefore did not produce meaningful results. Water was instead estimated to be saturated at the temperature at the outlet of the reflux condenser. Similarly, oxygen results were suspected to be low because the O₂ levels during the initial runs were 4 to 5 times below concentrations expected. This suspicion was verified when oxygen levels were taken with a standard oxygen meter and found to be above the range of the detector at >80% oxygen, compared with the 15% to 20% oxygen concentrations being determined by GC/MS. Oxygen was, therefore, determined by subtracting all other constituents from 100%. There is a possible fire hazard associated with this method of treatment, due to the high generation of oxygen. This issue must be addressed in the design. Limited fuel, lack of ignition sources, and saturated water vapor all serve to mitigate the fire hazard.

GC/MS gas analyses performed on syringe samples from the reactor headspace and at the outlet of the Dewar condenser have yielded only partial results. Initial results indicated that only the organics could be quantified using this method. Consequently, a monitor for CO₂ and O₂ was procured for test F-22 (80°C, 600 mL H₂O₂, 12 hr); future tests will include this monitor as well as on-line GC/MS sampling and automated analysis. Table 3-5 provides a summary of data collected for tests with valid gas data.

As expected, the majority of gas generated from the chemical oxidation process was O₂. Carbon dioxide was also generated along with water vapor, CO, and VOCs. The presence of CO₂ and CO in the off-gas indicates at least partial destruction of the organic constituents in the surrogate. The percentage of VOCs seen in the gas phase was lower than expected. The low concentrations of VOCs in the off-gas appear to indicate that the DREs of the VOCs were due to destruction rather than volatilization; however, the sampling frequency for off-gas (5 min after injection of peroxide commenced and then every 30 min) was probably not frequent enough to capture the spike of VOCs as it flowed out of the system. The samples collected during the 80°C runs indicated the presence of VOCs only in the first few samples and were nondetectable for the rest of the tests.

The 80°C runs had particularly high oxygen generation. If all the peroxide was converted to oxygen, 71 g of oxygen would have been expected in the off-gas for test F-21 (80°C, 250 mL H₂O₂, 8 hr) and 142 g would have been expected in the off-gas for test F-16 (80°C, 500 mL H₂O₂, 12 hr). The amount of O₂ generated was 68.9 g (F-21) and 139 g (F-16) when the area under the curves in Figure 3-3 are calculated. This indicates that about 96–98% of the peroxide is converted to oxygen and does very little to chemically oxidize the surrogate.

3.1.6 Supplemental Observations and Analyses

Besides collecting data to support the TOs, other data were collected to better understand the chemical oxidation process for V-tank waste. Also during the testing, observations were made that did not directly relate to the TOs. These observations and results from additional analyses are discussed in the following sections.

3.1.6.1 Observations. The overall mass balance closures for each test run have been very good, ranging between 96.6% and 99.9%. The mass balance closure for run MV was 89%. Oxygen was injected during the run to simulate peroxide decomposition; however, the injection line plugged periodically and prevented quantifying the gas flow accurately.

Table 3-5. Summary of gas generation data for selected tests.

Test Run	Test Conditions	O ₂ Generated (g)	CO ₂ Generated (g)	H ₂ O Generated (g)	CO Generated (g)	TCE Generated (g)	TCA Generated (g)	PCE Generated (g)	Total Gas Generated (g)	% of TCE Feed in Gas	% of TCA Feed in Gas	% of PCE Feed in Gas
F-6	40°C, 500 mL, 8 hr	10.1	0.026	0.249	0.016	0.011	0.001	0.006	10.4	1.3%	0.84%	6.0%
F-13	40°C, 400 mL, 12 hr	15.2	0.061	0.38	0.0002	0.014	0.0003	0.001	15.6	0.16%	0.99%	0.29%
F-21	80°C, 250 mL, 8 hr	68.9	0.538	1.71	0.002	0.009	0.0009	0.002	71.1	1.03%	1.15%	2.06%
F-16	80°C, 500 mL, 12 hr	139	0.233	3.44	0.006	0.0002	0	0.0003	142.8	0.02%	0%	0.44%

Observation of cooled product from the formal 80°C runs revealed a three-phase system with a sheen of oil on the surface; an aqueous phase that looked like a cloudy brine; and a settled, red, solid phase on the bottom of the flask. Trichloroethylene (TCE) and mercury vapors were detectable by Draeger tube in the headspace of the cooled flask. Titration tests indicated no substantial residual hydrogen peroxide in the product (i.e., well below 2% by weight, and commonly less than <0.1% by weight). The surrogate contained the full inventory of organics in a separate phase. The centrifuged, cooled product aqueous phase was nearly clear. The destruction of the organic phase, the clarity of the aqueous phase, and the fine, silty nature of the settled solids lead us to suspect that there were no CFTs remaining in the solids.

The reaction product from the two 40°C test runs was a thick slurry that would settle, but was easily resuspended. When settled, an oil layer was evident, containing entrained particulate. Product centrifugation under standard conditions (2,500 rpm for 20 min at 25±1°C) failed to attain the multiphase separation described for the 80°C runs. The cause may be due to turbulent mixing of the slurry by vigorous gas release from continuing decomposition of the residual peroxide during the 40°C tests. Subsequently, the concentration of residual peroxide was estimated at greater than 35% by weight.

As peroxide was added to all the 80°C runs, the reactor temperature increased to about 89°C and remained there for at least an hour after peroxide injection was complete. There was neither rapid rise in temperature, nor fluctuations, as had been seen in the beaker tests. Such thermal stability may be due to the reflux condenser removing heat and draining cooled condensate back into the reaction flask or, it may be due to rapid decomposition of the peroxide. There was some evidence of slight temperature fluctuation occurring later in a few of the runs.

3.1.7 Supplemental Chemical Analysis

Small (ca. 40 mL) aliquots of oxidized slurry were sent to BWXT for formal determination of residual levels of the volatile and semivolatile CFTs. The results from these analyses were used to calculate the contaminant-specific DREs. In addition, other laboratory methods were used to assess the degree of contaminant destruction using Fenton's reagent. These methods included:

- Presence (or absence) of select organic functional groups via qualitative "spot" tests
- Determination of chloride ion plus oil and grease levels via colorimetric and gravimetric methods, respectively
- Determination of headspace TCE and mercury levels (within the reaction flask) using Draeger tubes and Jerome 431-X mercury vapor analyzer, respectively
- Analysis of VOCs in centrifuged slurry plus Dewar condensate using EPA Methods 5030/8260B (Refs. 8, 9) and SVOCs using EPA Methods 3510C/525.2 (Refs. 10, 11).

The results from these evaluations are discussed below.

3.1.7.1 Spot Tests. MSE Technology hypothesized that partial oxidation of the oils and/or CFTs would produce compounds containing alcohol (OH), aldehyde (COH), and carboxylic acid (COOH) groups. The respective methods used to detect these groups were: chromic anhydride (Jones' Oxidation) for primary/secondary OH, Fuchsin-aldehyde (Schiff's) reagent for COH, and sodium bicarbonate/ CO_2 evolution for COOH.

Alcohol and COOH groups were detected only in Test Runs F-2A and F-4. Both experiments used 400 mL H_2O_2 and 8 hr at prescribed temperature (i.e., 40°C for F-2A and 80°C for F-4). The treated slurries from F-2A and F-4 exhibited residual peroxide levels of 22.5 and between 0.2% to 2% w/w, respectively. Thus, it is uncertain whether such "hits" represent compounds present in the untreated slurry or are indeed reaction products. The spot tests gave positive results throughout the Fenton's campaign, when standards (e.g., methanol, formalin) were used. Furthermore, the chromatograms from Test Runs F-16 (80°C, 500 mL H_2O_2 , 12 hr), F-21 (80°C, 250 mL H_2O_2 , 8 hr), and F-22 (80°C, 600 mL H_2O_2 , 12 hr) indicated the presence of the three functional groups (e.g., n-butanol, benzaldehyde, and benzoic acid). Given the undetects in the 500-mL H_2O_2 tests, MSE Technology suggests that the concentrations of these groups (regardless of origin) are too low to be identified in treated slurry.

CO_2 should represent the largest portion of the "oxidized carbon" fraction, followed by carboxylic acids (if the treatment reaction goes nearly to conversion). However, regardless of reaction completion, one can expect to see some aldehydes and alcohols as well. The latter fractional groups were detected occasionally in the Fenton's runs, but MSE suspects the concentrations produced were often below the respective method detection limit.

3.1.7.2 Chloride Ion Plus Oil and Grease. Chloride ion levels were determined colorimetrically via a ferric-thiocyanate complex, wherein the intensity of the color formation is proportional to the Cl^- concentration (at 480 nm). As peroxide levels > 2 mg/L interfere with ("bleach") this reaction, samples are pretreated with sodium arsenite to remove (reduce) residual H_2O_2 .

MSE Technology hypothesized the Cl^- levels would increase in treated slurry, proportional to the degree of H_2O_2 - peroxidation of the chlorinated CFTs. In such cases, it was also expected that residual peroxide levels would be $\leq 0.1\%$ w/w (i.e., oxidative treatment consumed the H_2O_2 delivered to the slurry); however, the analytical results to date indicate an increase in Cl^- levels with increasing H_2O_2 concentrations. For example, the F-6 run (40°C, 500 mL H_2O_2 , 8 hr) had 3,600 mg/L Cl^- and $\geq 35\%$ w/w H_2O_2 , while F-10 (80°C, 500 mL H_2O_2 , 12 hr) had 48 mg/L Cl^- and between 0.1% to 2% w/w H_2O_2 . The F-1B "blank" (80°C, 0 mL H_2O_2 , 8 hr) had a reported Cl^- concentration of 29.0 mg/L. Thus, MSE Technology suggests that analytical interferences exist in either the treated slurry or in the arsenite salt (Cl assay \cong 300 ppm), precluding accurate measurement of Cl^- ion. In follow-on work, an alternate analytical method (e.g., ion chromatography) will be used for chloride determination.

Samples of treated slurry from test runs F-16 (80°C, 500 mL, 12 hr), F-21 (80°C, 250 mL, 8 hr), and F-22 (80°C, 600 mL, 12 hr), plus standards containing known quantities of oils were submitted to the HKM Engineering Analytical Laboratory for oil and grease (o/g) analyses. Essentially, the samples are acidified, o/g extracted into hexadecane, and the solvent is then evaporated. Residual o/g is determined by weighing, and weight percent o/g calculated from the initial sample weight. Recovery of the o/g standard was 86.7%. The o/g results for F-16, F-21, and F-22 were 1080; 2740; and 546 mg/L, respectively. These results indicate increased oil destruction with increasing peroxide dosing and treatment time.

Oil-water separation was suggested very early in the project planning (as was VOC sparging), but both of these ideas were rejected. In regards to oil effects on contaminant of concern (COC) treatment, it appears that oil ultimately disappears along with the other contaminants (e.g., BEHP). Thus, oxidation of the oily materials appears to be necessary to lower the COC to acceptable levels.

3.1.7.3 Headspace TCE and Mercury. The concentrations of these parameters were determined in the headspace above the treated slurry the morning after each test run; handheld, occupational health/safety-type instruments were used to make these measurements. No clear pattern regarding parameter concentrations vs. treatment intensity (i.e., increasing time, temperature, H₂O₂ dosing) was observed. For example, the highest (> 100 ppmv) levels of TCE were observed in Test Runs F-9 and F-9A (80°C, ≥ 400 mL H₂O₂, 8 hr), wherein chilled water to the reflux condenser was turned off overnight. On the other hand, high (> 0.999 mg/m³) mercury levels were observed in the F-8, F-12 (80°C, 500 mL H₂O₂, 12 hr), and F-22 (80°C, 600 mL H₂O₂, 12 hr) test runs. All of these tests used ≥ 500 mL H₂O₂ for ≥ 8 hr and at 80°C; the chiller was off overnight for the F-8 run only. It is interesting to note that headspace TCE in the F-8 run was < 1 ppmv, of similar magnitude to that reported in the method validation (MV) run, 1 to 2 ppmv. The MV run was set at 80°C and 8 hr, with no peroxide addition; the chiller was turned off overnight (before sampling). Thus, the present data cannot be used to assess the potential for VOC destruction by Fenton's reagent. Similarly, no quantitation of potential conversion of elemental mercury (volatile) to aqueous forms (nonvolatile) can be offered, either.

3.1.7.4 VOC/SVOC Analyses by HKM Engineering Analytical Laboratory (Butte, MT). Inspection of the presently available VOA data does not indicate any relationship between solvent concentration(s) and treatment intensity. For example, test runs F-5 and F-9A (80°C, 500 mL H₂O₂, 8 hr) used the same conditions (80°C, 500 mL H₂O₂, 8 hr), yet TCE levels in centrifuged slurry were 19 and 454 µg/L, respectively; the TCE concentration in Run F-8 (same conditions as above) was 33 µg/L. In the second example, TCE in Test Run F-10 (80°C, 400 mL H₂O₂, 12 hr) was 23 µg/L, while 379 µg/L TCE was reported for Test Run F-12 (80°C, 500 mL H₂O₂, 12 hr). The likelihood of solvent carryover (from slurry) is evident from the F-10 (80°C, 400 mL H₂O₂, 12 hr) run, wherein TCE concentration in Dewar condensate was 164 µg/L (versus 23 in the reaction flask). A second example involves the F-16 (80°C, 500 mL H₂O₂, 12 hr) run, wherein the centrifuged slurry contained approximately 7 µg/L TCE versus 392 µg/L TCE observed in the condensate. It is also interesting that 1,047 µg/L BEHP was observed in Dewar condensate from the F-5 test run.

The data from BWXT was of acceptable quality. Matrix spike/matrix spike duplicate (MS/MSD), laboratory control standards (LCS) (e.g., bromofluorobenzene), and surrogate recoveries (e.g., chlorobenzene-d₅) for VOAs were acceptable. Terphenyl-d₁₄ recoveries were generally low, which resulted in higher BEHP concentrations than reported; however, the sample group of greatest concern (i.e., test runs F-9A [80°C, 500 mL H₂O₂, 8 hr], 10, and 12) were reextracted, with surrogate recoveries all within the acceptable range. The MS/MSD plus LCS recoveries for HCB were acceptable. The recoveries of decachloro-biphenyl and tetrachloro-m-xylene were occasionally low, but the overall results for the Arochlor 1260 analyses were acceptable.

The VOA data from the HKM Engineering Analytical Laboratory had LCS and surrogate recoveries within the acceptable (80–120%) quality control (QC) range, even for tenfold dilutions. The SVOCs analytical data also were acceptable (e.g., recoveries of perylene-d₁₂, triphenyl phosphate within the 80–120% range).

3.2 Definitive Test Runs

The purpose of the B-1A and B-1B tests was to determine the destruction efficiency of the surrogate V-tank waste using Fenton's reagent, to obtain further data on volatilization of VOCs from the surrogate before and during reaction, and to process sufficient surrogate to allow intermediate sampling and reprocessing of the remainder.

The B-1A run was to replicate to some extent the previous run, F-21. F-21 processed 150 g of surrogate with 250 mL of 50% hydrogen peroxide at an initial temperature of 80°C for 8 hr. All contaminants of concern were destroyed to below their UTS concentrations in Test F-21.

To better understand the capability of the Fenton's reagent as it had been applied throughout the project, the total quantity of the surrogate was increased, the proportional quantities of various organic compounds in the surrogate were increased, and several compounds were added to the surrogate.

For run B-1A, the target quantity of the surrogate was increased to 300 g, as compared to the nominal 150 g of the previous tests. The quantities of the inorganic solids were doubled; TCE, PCE, TCA and HCB were doubled also.

The quantity of biphenyl was made equal to HCB to allow a better determination of its DRE.

The quantity of BEHP was increased from about 166 mg to near 2 g. BEHP has been found to be generally the most refractory of the organic compounds in the surrogate. By adding more than an order of magnitude to the quantity of BIS, it was hoped that some insight into its degradation would be obtained.

New compounds added to the surrogate were benzene, ortho-cresol, para-cresol, phenol, and naphthalene. These compounds may be constituents of the sludge in the V-tanks or they may be degradation products from treating the sludge. To determine the effect of Fenton's treatment on the additional species and to ascertain if they would be destroyed adequately, O-cresol was added to the surrogate at nearly 2 g, and the other new constituents were added at 150 mg target quantities.

Reiterating, run B-1A doubled the total surrogate quantity and used 500 mL of peroxide. The test conditions of B-1A effectively duplicated a run that injected peroxide in the same proportion (run F-21). However, run B-1A increased the organic compound loading from 4.19 g of oil and 1.19 g of other organic compounds (for F-21) to 8.38 g of oil and 6.94 g of other organic compounds. For B-1A, the hydrogen peroxide (100%) to total organics ratio was 19.6 to 1, by weight. For run F-21, the peroxide to organics ratio was 23.2 to 1, or about 18% higher than run B-1A.

In considering the results of B-1A, it must be noted that the several new organic species in B-1A may have preferentially reacted with peroxide. Some of the new compounds may be easier to react with, and the resulting products may be due to selectivity effects rather than overall reaction conversion.

Concentration effects may have also occurred: the non-oil, organic concentration increased by almost a factor of six, while the peroxide to organics ratio dropped from 23.2/1 to 19.6/1.

In other words, by increasing species and concentrations of constituents from run F-21 to run B-1A, the number of reactions, the rates of those reactions, the reaction orders, and the mechanisms involved may be changed. Conclusions drawn from the results are then, of necessity, qualitative and speculative except for the measured destruction of the species of concern.

B-1A was also designed to provide additional knowledge on volatilization behavior of the solvents (TCE, PCE and TCA).

In past tests, even though make-gas samples for GC/MS analysis were taken every thirty minutes, it has not been possible to close the mass balances for the three solvents. The amount of solvent accounted for by flow from the apparatus has been less than 10%. Neither has it been possible to achieve valid chloride analyses in the product liquor, due to unforeseen interferences in the analytical method. Thus, it was not possible to account for mineralization of the solvents.

To try to quantify the fate of the chlorinated solvents, Tedlar bags were attached to the apparatus exit gas line to collect the entire gas make for the initial period of the run, including heat up. The gas in the Tedlar bags was then analyzed for solvents, and the volume of gas collected in the bags was approximated, which precluded measuring accurate gas flow rates for the initial period of the run. Gas rates were estimated by averaging the volume in each Tedlar bag over the time period of gas collection.

The purpose of run B-1B was to demonstrate that a product from a previous run could be reprocessed if it did not meet UTS requirements. The deliberate, massive increase in COCs for run B-1A was, in part, to have measurable concentrations of unreacted components in its product to allow further measurement of DRE in run B-1B.

The quantity of hydrogen peroxide used for run B-1B was 415 ml of 50% peroxide. The quantity of hydrogen peroxide for run B-1B was designed to keep the ratio of hydrogen peroxide to surrogate for B-1B equal to that for B-1A. That is, 600 g of peroxide were charged to the 304 g of initial B-1A charge for a ratio of $600/304 = 1.97$; 498 g of peroxide to 253 g of B-1a residual was charged to B-1B, for a ratio of $498/253 = 1.97$.

The purpose of keeping the peroxide ratios constant was to simulate an extended run with intermediate sampling. The extent of reaction would be determined at the end of 8 hr. If some of the 8-hr run products did not meet UTS, the run would be resumed, adding peroxide on the previous schedule, to evaluate whether the concentration of the refractory COCs would be reduced to the required limits.

3.2.1 Results

3.2.1.1 Run B-1A. The operating conditions for Run B-1A were 304 g of surrogate charged to the reaction flask, 500 mL of hydrogen peroxide injected, an average run temperature of 89.6°C, and a run time of 9 hr (8 hr after the beginning of injection).

Hydrogen peroxide was injected at 10 mL/min for the first ten minutes of the run, followed by 400 mL injected at a rate of 2 mL/min. The rate of initial peroxide versus surrogate quantity for the first ten minutes of the run was proportionally the same as in the previous, “F” series runs, (i.e., 10 mL/min/300 g = 5 mL/min/150 g). The injection rate for the remainder of the injection period was 2 mL/min, effectively halving the peroxide rate to surrogate mass of the “F” runs (2/300 versus 2/150). Halving the peroxide injection rate doubled the injection time.

The final product slurry weighed about 786 g; its volume was 740 mL. The make gas weighed about 138 g; the average make gas rate was 262 accm and the maximum rate was 1,145 accm (1.245 g/min). The make gas was primarily oxygen.

The overall mass balance closure was 96.5%. The “F” series tests had better overall closures (typically $\geq 98\%$); since B-1A used Tedlar bags to collect gas for the first hour of the run, gas rates were somewhat uncertain and probably account for the lower closure.

Quantitative and calculated results are tabulated in the accompanying Excel spreadsheet for the run (Appendix C). Significant results are discussed below, mainly concerning DRE and solvent volatilization.

Table 3-6 lists the quantitative results of the run for the organic compounds added to the surrogate. Most of the compounds have UTSS and are known to exist in the V-tanks’ sludge. The “other” compounds in Table 3-6 are surrogates for characteristic compounds in the sludge, or were perhaps intermediates resulting from treatment of the sludge that were added to see if the Fenton’s reaction would also treat them.

Table 3-6. Run B-1A destruction/removal efficiency.

Component	Feed (mg)	Product (mg)	Product (mg/kg)	DRE (%)	UTS (mg/kg)
Oils	15,340 ^a	12,580	16,000	17.98	N/A
Arochlor 1260	100	10.193	13,000	89.81	10
TCE	1,705	1.686	2.150	99.90	6
PCE	149.7	0.199	0.254 J ^b	99.87	6
TCA	181.3	1.560	1.990 U ^c	99.14	6
BEHP	1,965.4	477.9	609.5	75.68	28
Benzene	154	1.560	1.990 U	98.99	10
HCB	152.0	20.779	26.500	86.33	10
Biphenyl	152.8	3.921	5.000 U	97.43	N/A
o-Cresol	1,813.2	3.921	5.000 U	99.78	5.6
p-Cresol	173.5	3.921	5.000 U	97.74	5.6
Phenol	151.8	3.921	5.000 U	97.42	5.6
Naphthalene	153	3.921	5.000 U	97.44	5.6

a. Oil and Grease in this case includes all organic species charged to the reaction flask.

b. The quality assurance symbol “J” indicates that the species analyzed was detected at a concentration below the quantification limit.

c. The quality assurance symbol “U” indicates that the species analyzed was not detected. The quantification limit is shown. The product species mass is the maximum possible and the DRE shown is the minimum. Often, half of the quantification limit will be used to calculate DRE and product species mass.

As shown in Table 3-6, Arochlor and BEHP were not reduced to below their UTS requirements in the product slurry. TCE was detectable above the quantification limits of the analyses. HCB, which is used as a surrogate for PCBs, was not reduced to its corresponding UTS of 10 mg/kg. All other compounds were undetectable at the quantification limits (although PCE was detected below the limit) at concentrations below their respective UTS limits.

Both BEHP and Arochlor had been reduced to below the UTS requirements in run F-21. Run B-1A was somewhat of a scale-up of F-21, as was explained previously. Arochlor had been treated below the UTS limit in the other “F” series runs to which it was added (F-16 and F-22); however, BEHP met the treatment standard in only two out of the five additional runs at 80°C and over 250 mL of peroxide. BEHP appears to be the most refractory of the compounds in the V-tank surrogate.

The oil and grease analysis for the B-1A run indicated that only about 17% of the total organic loading was removed. We considered the entire organics loading to be part of the oil and grease in the sample; that is, all of the charged organic compounds would probably have been extracted by the hexadecane used in the analytical method. The total charge of organic compounds for test B-1A was about 15.3 g; the amount of oil and grease left in the product was about 12.6 g, according to the analysis, giving the 17% DRE.

From the DRE results for TCE, BEHP and o-cresol, about 5 g of organic compound would be expected to have disappeared during the run, leading to a DRE of over 30%. This discrepancy in the amount of organic reacted in the run may be due to either sampling inefficiency or to lack of mineralization.

Since the products of the Fenton's reaction are very heterogeneous, obtaining a representative sample, especially for oil and grease analysis, is difficult. It was noted that the product slurry for run B-1A contained three distinct layers; with only one sample analyzed, no data is available to show if the oil and grease analysis varied widely.

If the organic compounds were not totally mineralized, that is, the COCs formed other organic species rather than being totally oxidized, then the oil and grease analysis would have accounted for the degradation products. Thus, there may have truly been only 17% instead of 30% of the organic charge reduced in the run. This assessment is confounded by the likelihood of formation of partial oxidation products that are more polar, and subsequently more water-soluble, than the parent compounds in oil.

The second major objective of the B-1A run was to determine whether the chlorinated solvents volatilized or were destroyed in the Fenton's reaction.

To better capture solvents leaving the system by vaporization, 1-L Tedlar bags were attached successively to the make gas line. This was done instead of measuring the gas flow rate with bubble meters and taking syringe samples for GC/MS analysis.

The first Tedlar bag was attached to the gas line before the solvents were charged to the reaction flask and while the flask was at room temperature.

After the solvents were charged to the flask, the silicon heating oil was allowed to flow into the heating jacket and the contents brought up to temperature over the course of about an hour. Once the charge was at 80°C for 15 min, hydrogen peroxide injection began.

The first bag was switched about 35 min after heat up began. The second bag was on for 27 min and straddled the beginning of injection. The third bag was on for 7 min; the fourth for 2 min; the fifth for 3 min and the sixth for 1 min. All except the first bag filled to their 1-L capacity during the time they were on the make-gas line. It took 2–4 min to change out the bags, during which additional gas was not collected.

Table 3-7 lists the bag analyses and estimated quantities. If only the bags are quantified, about 56% of the TCA charged to the flask can be accounted for. If the time intervals between bag change-outs are considered with the concentrations and flow rates interpolated from the bags, all of the TCA can be assumed to have evaporated from the flask as well as about 9% of the TCE. It appears that PCE remains in the liquor, possibly due to a vapor pressure lower than exhibited by TCE and TCA.

Table 3-7. B-1A make gas analysis, Tedlar bags.

Bag Number	TCE (ppm _v)	PCE (ppm _v)	TCA (ppm _v)	Volume (mL)	Mass (gmol)
1 (Start to 10:41)	2.1	0	0	76	0.0026
2 (10:42 to 11:10)	2.3	0	0	925	0.0322
3 (11:16 to 11:23)	240	0	1483	852	0.0297
4 (11:29 to 11:31)	1139	0	8879	855	0.0298
5 (11:35 to 11:38)	11922	0	5896	1004	0.0350
6 (11:42 to 11:43)	4192	0	7221	1003	0.0349

Using the ppm_v of each component and the moles of gas estimated to be in the bags, the following component masses are accounted for:

Component	Charge (g)	Bag Sum (g)	Found/Charge (%)
TCE	1.705	0.079	4.6
PCE	0.1497	0	0
TCA	0.1813	0.102	56

Several minutes would elapse between removing one Tedlar bag and replacing it with the next. For the “gaps” between bag samples, gas flow rates were estimated from the bag volumes and collection times. Average flow rates and average concentrations between Tedlar bags were used to estimate the solvent volatilized during the change-out times. The results were revised to the following:

Component	Charge (g)	Bag Sum (g)	“Gap” Sum (g)	Found/Charge (%)
TCE	1.705	0.079	0.066	9
PCE	0.1497	0	0	0
TCA	0.1813	0.102	0.100	111

As shown above, TCA is over-accounted for; however, the trend is apparent. TCA appears to leave the surrogate quantitatively; TCE volatilizes to some extent, while PCE remains in the charge. These trends are expected, given the relative vapor pressures of these solvents.

An interesting observation is that all the TCA in the surrogate charge was soluble in the 240 g of water charged to the flask. The solubility of the other two solvents is much less, as shown below. In the complex mixture of organic compounds that were charged to run B-1A, it is unknown whether the differences in solubility are significant.

Component	Charge (g)	Solubility (g/L)	Soluble Amount (g)	Soluble Fraction (%)
TCE	1.705	1.4	0.336	19.7
PCE	0.1497	0.15	0.036	24.0
TCA	0.1813	1.5	0.359	198

The results of run B-1A are summarized below.

Arochlor 1260 and BEHP were charged to the reaction flask in massive excess relative to their concentrations used in previous tests, and to their maximum concentrations anticipated for the V-tanks’ slurry. In the product slurry, Arochlor was reduced by 89.1% to 13 mg/kg; not quite the 10 mg/kg required to meet its UTS. BEHP was reduced by 75.68%; the product concentration of 609.5 mg/kg was well above the required UTS requirement of 28 mg/kg. HCB was reduced by 86% to a product concentration of 26.5 mg/kg, above its UTS of 10 mg/kg.

All other organic compounds were reduced to below their UTS standards or to below the quantification limit of the analytical methods. O-cresol was charged to near the same quantity as BEHP and was removed to below its quantification limit.

Oil and grease analysis showed that about 18% of the total organic loading of the surrogate disappeared during run B-1A. This appears to indicate that the disappearance of major contaminants does not imply that they were entirely mineralized; they may have been oxidized to different, hexadecane-soluble compounds that would be included in the results of the oil and grease analysis.

3.2.2 B-1B Results

The operating conditions for Run B-1B were 257.2 g of surrogate charged to the reaction flask, 415 mL of hydrogen peroxide injected, an average run temperature of 88.7°C, and a run time of 10.75 hr.

Hydrogen peroxide was injected at 5 mL/min for the first ten minutes of the run, followed by injection at a rate of 2 mL/min until a total of 415 mL of peroxide was injected.

The final product slurry weighed about 652 g; its volume was 628 mL. The make gas weighed about 95.2 g; the average make gas rate was 150 accm, and maximum gas rate was 263 accm (0.275 g/min). The make gas was primarily oxygen.

The overall mass balance closure was 97%.

Quantitative and calculated results are tabulated in the Excel spreadsheet for the run (Appendix C).

The column in Table 3-8 entitled “feed” is not the mass of each particular species in the charge to B-1B as would be measured by chemical analysis. The feed quantity is calculated by proportioning the mass of B-1B charge (B-1A product) to the initial charge of B-1A, and multiplying the resulting number by the mass of each species charged to B-1A. The resulting “feed” quantities charged to B-1B for each species is an attempt to quantify the amount of each compound that would be exposed to both the A and B runs, and allow a calculation of an overall DRE resulting from both runs (a sequential or series DRE). This method may not have any real meaning. The results of run B-1B that are most important are the concentrations of the COCs, and whether the product concentration of each meets UTS requirements.

Table 3-8. Run B-1B destruction/removal efficiency.

Component	Feed (mg)	Product (mg)	Product (mg/kg)	DRE (%)	UTS (mg/kg)
Oils	12,900 ^a	73	112	99.44	N/A
Arochlor 1260	84	2.543	3.900	96.99	10
TCE	1,438	1.242	1.905 U	99.91	6
PCE	126	1.242	1.905 U	99.02	6
TCA	153	1.242	1.905 U ^b	99.19	6
BEHP	1,658	202.1	310	87.81	28
Benzene	130	1.242	1.905 U	99.04	10
HCB	128	4.454	6.830	96.53	10
Biphenyl	129	3.218	4.935 U	97.50	N/A
o-Cresol	1,530	3.218	4.935 U	99.79	5.6
p-Cresol	146	3.218	4.935 U	97.80	5.6
Phenol	128	3.218	4.935 U	97.49	6.2
Naphthalene	129	3.218	4.935 U	97.51	5.6

a. Oil and grease in this case includes all organic species charged to the reaction flask.

b. The quality assurance symbol “U” indicates that the species analyzed was not detected. The quantification limit is shown. The product species mass is the maximum possible and the DRE shown is the minimum. Often, half of the quantification limit will be used to calculate DRE and product species mass.

An attempt to calculate DRE by taking the concentration of each COC measured in the product of run B-1A and proportioning the product mass between the charge to B-1B and the sample taken for analysis gave negative DREs for run B-1B in many instances. This is shown on page 7 of the B-1B spreadsheet. The negative DREs are due to using the B-1A detection limits to calculate the mass of charge to the next run. In some cases, the B-1B product species appeared to be in higher quantities than in the B-1A products.

In Table 3-8, the only species worth considering are oil and grease, Arochlor, BEHP and HCB. All other species, except for TCE, are reported below their quantification limits. Run B-1B reduced Arochlor and HCB to below their respective UTS of 10 mg/kg.

BEHP, the most refractory of the organic surrogates, still had not been reduced to its UTS standard. About 75% of the BEHP was converted in the first run, and the second run converted about 15% more; to achieve the required UTS concentration, it may require an additional quantity of peroxide for several more hours.

Of the seven "F" series runs at 80°C, three met UTS concentration requirements and one additional run was within 0.5 mg/kg of the UTS requirement of 28 mg/kg for BEHP removal. The "F" runs were charged with about 166 mg of BEHP and would achieve nearly 90% DRE. The B-1B product has about 202 mg of residual BEHP; by further reaction, the compound should be reduced to acceptable treatment standards.

There are further points that may be significant with regards to BEHP. An additional increment of iron catalyst, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, was not added to run B-1B; the residual from run B-1A was felt to be sufficient to react with the additional peroxide. Another increment of iron may have increased the rate of reaction for BEHP destruction.

Peroxide injection for run B-1B was not exactly similar to run B-1A. Run B-1A injected 100 mL in 10 min; run B-1B injected 50 mL in the first 10 min. There may have been some effect on reaction by this change. However, as shown on page 8 of the spreadsheet, the peroxide balance for the respective runs show that the peroxide available for reaction for run B-1B averaged 88 g, versus 32 g for run B-1A. The concentration of peroxide in the slurry on the average for the second run was higher, which should have increased the reaction rate.

The above two paragraphs may mean nothing in light of the oil and grease analysis for run B-1B. Oil and grease was removed to 99.44%, or 73 mg residual. If oil and grease analysis truly accounts for all organic compounds, the results contradict the 202 mg residual BEHP. However, the oil and grease sample is typically small and could be biased (i.e., unrepresentative of total slurry volume), and the resulting analysis could vary by a high percentage.

The physical appearance of the final B-1B product indicated only a very slight sheen of oil. It appears that Fenton's reaction destroyed all other COCs and the oil, and that the remainder on the surface of the product slurry could consist mainly of the residual BEHP.

There was residual TCE in the product from Run B-1A (1.7 mg product from a 1,700 mg charge). Tedlar bags for gas analysis were attached to the make-gas line at the beginning of run B-1B similar as had been done for the B-1A run. As can be seen in the spreadsheet, essentially no volatiles were found either in the Tedlar bags or in the syringe samples of the make gas. Run B-1B had BEHP, oils and possibly organic intermediates to react with, and all but the most refractory BEHP appears to have been treated.